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ELEMENTS OF CHEMISTRY.

ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.

BY

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SECOND EDITION, WITH ADDITIONS.

PART III.

ORGANIC CHEMISTRY.

LONDON:
PARKER, SON, AND BOURN, W
1862.

LONDON:
SAVILL AND EDWARDS, PRINTERS, CHANDOS STREET,
COVENT GARDEN.

PREFACE TO THE SECOND EDITION.

THE principal objects which the author proposed to himself in the present treatise will probably be best explained by the following extracts from the Preface to the first edition.

'In the work of which the present volume forms the third and concluding portion, it has been the aim of the author to give the leading facts and doctrines of chemical science, in as concise a form as possible, without sacrificing clearness and accuracy to brevity. But in order that the reader may be enabled to refer to original sources when further information is needed, references have been given to the papers from which the more important details have been obtained, particularly to the recent memoirs on organic chemistry.

'It will be observed that in the arrangement of the present volume, free use has been made of the system of classification in homologous series, which was employed with such admirable results by the late highly gifted M. Gerhardt, whose early removal from the scene of his indefatigable and successful labours the scientific community have had so recently to deplore.

'The general method of classification adopted by that eminent chemist in his *Traité de Chimie Organique,* excellent as it is in many respects for the advanced cultivator of the science, is not, however, well adapted to the plan of a didactic work like the present; and it was judged preferable, after a preliminary sketch of the methods of investigation and classification employed, to commence the detailed description of the products of organic chemistry with that of a few of the best known and most familiar compounds derived from the vegetable kingdom, although their composition is less simple than that of many other organic substances: for this reason sugar, starch, and vegetable fibre were made the starting point; and from them the transition was easy to the processes of fermentation, and the comprehensive group of alcohols, and their derivatives the ethers and allied compounds.

'In treating these various classes of compounds, the author preferred to examine successively the different members of each homologous group, before passing to the consideration of the derivatives from the typical or leading member of each group. For instance, in the case of ordinary alcohol, instead of describing ether, aldehyd, and acetic acid in succession,—the different varieties of alcohol, such as wood spirit, fousel oil, &c., are first described; then the series of the vinic acids, and then that of the ethers. By thus presenting the different members of the same homologous series in succession to the student (see p. 34) he is enabled to trace more readily their similarities and their differences, and to note the general method adopted in their preparation, than if his attention were distracted by passing to other bodies of totally different character and properties. This plan conduces to brevity as well as to clearness, and facilitates the description of the various series from a more general point of view, than would be readily practicable, if the arrangement followed by most writers since the appearance of

Liebig's classical work on organic chemistry were followed.

'The homologous and the collateral series may be compared to a number of ladders placed side by side against a house. The terms of a homologous series succeed each other like the rounds of a ladder, whilst the terms of the derived and collateral series are like those of a second or a third ladder placed by the side of the first. It is safer and easier to ascend or to descend the steps of each ladder in succession, than to step across from one ladder to the other.

'In the nomenclature of the alcohols and their derivatives, the principle introduced in the case of the hydrocarbons by Berzelius, and more fully carried out by Gerhardt, has been followed, with the view of avoiding the confusion which would have been introduced into this portion of the subject, had the names which are frequently employed to designate them been retained; for example:—

$$\underbrace{\overbrace{C_8H_8}^{\text{Butylene.}}}_{\text{Tetrylene.}} \quad \underbrace{\overbrace{(C_8H_9)_2}^{\text{Butyl.}}}_{\text{Tetryl.}} \quad \underbrace{\overbrace{C_8H_7O_2}^{\text{Butyryl.}}}_{\text{Butyryl.}} \quad \underbrace{\overbrace{C_8H_9O,HO}^{\text{Butylic alcohol.}}}_{\text{Tetrylic alcohol.}} \quad \underbrace{\overbrace{HO,C_8H_7O_3,}^{\text{Butyric acid.}}}_{\text{Butyric acid.}}$$

the lower series of terms being those adopted in the present work; and in order to escape the confusion between *butyl* the radicle of the alcohol, and *butyryl* the radicle of butyric acid, the Greek term *tetryl* has been substituted for that of *butyl;* the series derived from the alcohol being thus distinguished from that derived from the acid. Names formed upon this principle, it is true, are often less euphonious than those which they are designed to displace; but it is better to sacrifice euphony than precision, and the new terms have the advantage of distinctly recalling the proportions of carbon which are present in the respective compounds indicated.

'It is necessary to remark that certain acids, particularly the carbonic, the sulphuric, and the sulphurous, are treated in the first and second portions of the work as though they were monobasic; whilst in the third part they are viewed as dibasic. At the same time it was stated (Part II., pp. 58, 162, 173, 866) that there are many circumstances which render it probable that the latter hypothesis is the more correct one. It appeared to be convenient to retain in the elementary portion of the work, the older view which regards these acids as monobasic, and which has been hitherto assumed in all treatises published previous to that of Gerhardt. The necessity for theoretical explanations at an early point in the work was thus obviated, and the simplicity in the formulæ usually adopted was preserved. In the complicated phenomena of organic chemistry, however, the results of experiment are more readily interpreted by assuming that these acids are dibasic.

'In the closing chapter of the work, a careful review of Kopp's researches upon atomic volumes and the boiling point of organic liquids, is given: and it is hoped that the comparison of the results of Andrews upon the heat of combination with those obtained by Favre and Silbermann upon the same subject, will be found of value and of interest to others besides the student.' . . . .

It is unnecessary to specify minutely the alterations which have been made in the second part of this work, as that volume has already been in the hands of the public for twelve months. Besides the numerous additions and emendations rendered necessary by the progress of science, the volume has been rendered more complete as a manual for reference by the introduction of statements of the centesimal composition of the different gases, as well as of the more important compound bodies generally.

The alterations in the present volume are more considerable. During the past four years the theory of polyatomic combinations has acquired rapid and important experimental illustration. It has therefore been carefully discussed and exemplified in the present edition; as will be seen by reference to the theory of types in the preliminary chapter, as well as to the sections on the diatomic and polyatomic alcohols, and to those on the amides and the compound ammonias.

The views of Gerhardt on the polybasic or multequivalent character of certain elements, and their important extensions in the hands of his successors, are also considered at some length in the preliminary chapter.

The interesting relations which have been discovered between many of the organic acids, such as the succinic, malic and tartaric, the gallic and salicylic, the lactic and propionic, are also indicated. Amongst the most important additions in the descriptive part of this volume may be mentioned the investigations of Berthelot on the saccharides and mannides; those by the same chemist on acetylene (which is identical with the klumene described in 1836 by Edmund Davy); the glycols and their ethers; the amidic acids, the study of which has explained the nature of glycocine and its homologues; the organic peroxides of Brodie; the nitrosulphides of Roussin; the researches of Strecker on guanine and the bases allied to it; besides numberless other additions to our knowledge which are incorporated in their respective places in the body of the work.

Since the appearance of the second volume of this treatise, Bunsen and Kirchhoff have published their remarkable discovery of the two new alkalies cæsia and rubidia, to which they were led by the application of the method of spectrum analysis; and the observations of Mr. Crookes by the same method have rendered it probable that new element more or less analogous to sulphur ists.

The author has again to acknowledge the kindn s friend Mr. Hadow, who has undergone the irk bour of reading the proof sheets of the entire work s aided materially in reducing the number of e hich are almost unavoidable in a work of this n d extent.

KING'S COLLEGE, LONDON,
November, 1861.

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PART III.

ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

§ I. *Analysis of Organic Compounds;*—§ II. *Principles of Classification;*—§ III. *Metamorphoses of Organic Compounds.*

(897) ORGANIC CHEMISTRY, in its primary signification, is that division of the science which treats of the chemistry of organized beings, and of the products of their chemical actions upon matter in its various forms.

It is important *in limine* to draw a clear distinction between *organic compounds* and *organized bodies.*

Organic compounds, like those derived from the mineral kingdom, possess a definite composition, and in many cases exhibit a perfectly definite crystalline structure. Bodies, such as sugar, oxalic acid, urea, taurin, and quinia, belong to this class; such substances are often spoken of as the *proximate principles* of animals and vegetables: many of them may be obtained from inorganic bodies by synthesis.

On the other hand, organized bodies, such as muscular tissue, nervous structure, cellulin, and ligneous fibre, never exhibit any tendency to crystalline structure, but show a rounded, vesicular, or fibrous configuration; and are so connected with each other as to form parts of a system, each of which is incomplete if severed from the remainder. Bodies such as these cannot be prepared synthetically: they are the result of the action of living bodies upon inanimate matter; a living body having the power of assimilating fresh particles, and of arranging them in the special form which characterizes the class to which the individual organism belongs.

The study of the chemical changes that occur during these transformations, constitutes *physiological chemistry,* the most difficult branch of the science. Its difficulty depends, however, not upon the obscurity which enshrouds the nature of life itself; for the essential nature of every description of force, and of the mysterious tie which exists between matter and force, has baffled the penetration of the profoundest philosophers, and belongs to an order of truths to which the human intellect probably may not be permitted in this sphere of its existence to attain.

The difficulty in the study of the chemical changes that occur in the living animal or plant depends rather upon the extreme delicacy of the arrangements by which these metamorphoses are effected; and upon the complicated nature of those arrangements, which are liable to injury from a multiplicity of causes that have hitherto eluded scrutiny. Other difficulties arise from the facility with which important changes are effected in the organism itself without being appreciable to human sense, save in their results, although they may even proceed so far as to occasion death. The ligature of a large artery or the section of a nerve effects an alteration which can be at once appreciated; but when an animal is poisoned by a fraction of a grain of aconitina or by a few drops of hydrocyanic acid, there is nothing to indicate to the anatomist, to the microscopic observer, or to the chemist, the mode in which these bodies operate in suddenly cutting short the life of the animal. The organization still appears to be perfect, yet the living laboratory no longer continues to perform its wonted operations, and the inanimate mass speedily falls under the dominion of ordinary chemical laws. In the living body, ordinary chemical affinities are suspended, and compounds are produced, which, when released from the influences under which they originated, quickly undergo fresh changes, which are manifested by the occurrence of putrefaction and decay, to which both animal and vegetable bodies are liable when they no longer form parts of the living frame. Occasional instances of instability, somewhat analogous to those exhibited by organized bodies, are seen in some of the compounds of inorganic chemistry; but this perpetual tendency to change is one of the distinguishing and essential characteristics of living bodies. When the plant or the animal is performing its functions in a healthy manner, these changes succeed each other in a defined and regular order; but if this sequence be modified, even in a slight degree, disease generally ensues, and when the alteration reaches a certain amount or degree, death is the speedy and inevitable consequence.

In the present work the attention of the reader will be only incidentally directed to the physiological portion of the subject, the main object being to exhibit the mutual relations which the different chemical compounds bear to each other, and to trace the laws of their formation. Even with these limitations the subject of organic chemistry is one of great extent and complexity.

(898) *Organic products* are composed of a small number of elements: yet such products present properties as much opposed to each other as it is possible to imagine; some constituting the daily food of man, others acting as direct and violent poisons: yet these very different bodies rarely consist of more than four elements, viz., carbon, hydrogen, nitrogen, and oxygen; a few contain minute proportions of sulphur and phosphorus, with certain earthy and saline matters.

The presence of carbon is so uniform in organic bodies, that generally one of the most convenient means of ascertaining if an unknown body be of organic origin, is to heat a fragment of it in a narrow test tube; the carbon is thus separated, and the substance becomes charred and blackened, except in a few cases where the material may be wholly volatilized without undergoing decomposition. Several of the essential oils, such as those of turpentine, elemi, juniper, and attar of roses, consist of carbon and hydrogen only: the same may be said of naphthalin, benzol, and the illuminating constituents of coal gas: but the larger number of organic bodies contain carbon, hydrogen, and oxygen; this occurs, for example, in the case of sugar, acetic acid, alcohol, the fixed oils, and the greater part of the proximate principles of vegetables. Nitrogen is superadded to these elements in many instances, though such compounds are of less frequent occurrence, except in highly organized portions of the plant or animal, such as the seed, or the muscular and other animal tissues; albumen, fibrin, indigo, quinia, and the vegetable alkalies generally, contain nitrogen as an essential component. The presence of nitrogen may in most cases be ascertained readily by heating a small fragment of the substance in a tube with hydrate of potash, when a distinct odour of ammonia is perceived.

The organs by which these various compounds are produced always contain small quantities of salts of the alkalies and earths, among which the compounds of potassium, sodium, calcium, and magnesium, in combination with chlorine, and with sulphuric, phosphoric, and silicic acids, are the most frequent: in rarer cases oxides of iron and manganese are met with, and in still rarer instances, fluorine, iodine, and bromine. The presence of certain of these saline bodies appears to be a condition as essential to the chemical activity of the growing plant or animal as that of carbon, of hydrogen, or of oxygen; for no organized tissue has ever been obtained from some of these saline substances. Besides these natural compounds of organic products, the chemist often artificially introduces other elements for the purpose of dissecting, as it were, these compounds, and of ascertaining the probable rational composition of the body under experiment. With this view he often produces new compounds which contain sulphur, phosphorus, chlorine, bromine, iodine, nitrous acid, or sulphuric acid; or he obtains others in which arsenic, antimony, zinc, and a variety of metallic bodies, are introduced into the original substance.

[illegible] *Organic and Inorganic Compounds.*—Many distinguished philosophers have attempted to draw the line which separates organic from inorganic chemistry. Thus, Laurent has termed organic chemistry 'the chemistry of carbon,' and Liebig has defined it as 'the chemistry of compound radicles.' Few persons, however, would be disposed with Laurent, to consider carbonic acid as an organic compound, and many chemists regard sulphurous acid, which is undoubtedly a compound inorganic substance, as the radicle of a somewhat numerous series of bodies of inorganic origin.

There is, in fact, no definite line of demarcation between inorganic and organic products. Amongst the productions of organized nature, acids, alkalies, salts, and other bodies are met with, similar in chemical functions to those derived from inanimate nature; and all organic compounds, when once formed, are subject to precisely the same chemical laws as those which regulate the combinations and decompositions of bodies confessedly inorganic; but the composition of the former being generally much more complicated than that of the latter, the balance of affinity in organic bodies is disturbed by slighter causes; and there are, consequently, an unnumbered variety of products generated by slight modifications of the various forces to which organic substances are subjected.

Still, for convenience sake, it is advisable to classify chemical compounds in some measure according to their origin; since those derived from the inorganic world, from the greater simplicity of their composition, afford to the student the most favourable instances for examining the fundamental laws of chemical combination, before he proceeds to the investigation of the more complicated products obtained from operations of the living vegetable or animal.

The number of organic compounds known to chemists is very great, and the list is perpetually undergoing increase; it therefore cannot excite surprise, if amongst them numerous instances of isomerism, metamerism, and polymerism (413) should occur.

The formation of *isomerides, metamerides,* and *polymerides,* as bodies which possess the same percentage composition may be termed, can only be accounted for by supposing that differences of chemical arrangement occur in these different cases. In some instances a rational explanation of the cause of difference may be given. A familiar example is afforded in the case of the three metamerides, propionic acid, acetate of methyl, and formic ether. These bodies are liquids, each of which contains $C_6H_6O_4$, they yield vapours of the same density, the latter two even have nearly the same boiling point and specific gravity; but there can be no doubt that they are all differently constituted. Propionic acid is one of the acids of the stearic series. The acetate of methyl is prepared by the action of acetic acid upon wood spirit, and acetic acid may be extracted from it by means of an alcoholic solution of potash, whilst wood spirit is liberated; formic ether is the result of an action of formic acid upon ordinary alcohol, and when treated with potash in the same way as the acetate of methyl, betrays its origin by yielding formic acid and alcohol. Each of these bodies must therefore be represented as possessing a different molecular constitution, thus:—

$$\overbrace{HO,C_6H_5O_3}^{\text{Propionic acid.}}=C_6H_6O_4\,; \quad \overbrace{C_2H_3O,C_4H_3O_3}^{\text{Acetate of Methyl.}}=C_6H_6O_4\,; \text{ and,}$$

$$\overbrace{C_4H_5O,C_2HO_3}^{\text{Formic Ether.}}=C_6H_6O_4.$$

In other cases, such for example as the ordinary sugar of fruits ($C_{12}H_{12}O_{12}$), no reasonable hypothesis of its composition has been offered; yet we know of the existence of several bodies isomeric with it, such as hydrated lactic and acetic acids, for which rational formulæ (282) are in common use.

Even in substances of comparatively simple composition, the difficulty of framing a conclusive theory of their molecular arrangement is very great, as may be seen by inspecting the following table, which represents a few of the views which have been taken respecting the nature of hydrated acetic acid:—

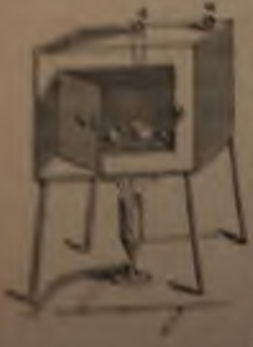
$C_4H_4O_4$ . . .	Hydrated Acetic Acid.	(Empirical formula.)
$HO,(C_4H_3)O_3$	Hydrate of Teroxide of Acetyl.	(Liebig.)
$\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$ . .	Water type theory	(Gerhardt.)
$HO,(C_2H_3)C_2O_3$	Methyloxalic Acid	(Kolbe.)
$HO,C_2(C_2H_3)O_3$	Methylformic Acid	(Wurtz.) (Gerhardt.)
$H,C_4H_3O_4$ . .	Binary theory	
$(C_4H_4)O_4$ . .	Nucleus theory.	

It must, however, be borne in mind, that conjectures such as these, as to the internal arrangement of organic bodies do but represent probabilities. We cannot, indeed, assert positively in any instance what the actual grouping of the component atoms may be, but we may infer, with reasonable confidence, that that grouping, be it what it may, is similar in allied or homologous [illegible] compounds. The rational formulæ which embody these views should therefore be regarded simply in the light of *memoria technica*; means by which facts may be riveted upon the memory, and by which analogies that otherwise would escape the notice of the observer may be traced; and, above all, as instruments by which that precision may be given to our ideas, which is so essential to the reception and advancement of solid philosophical knowledge.

§ I. ON THE ANALYSIS OF ORGANIC COMPOUNDS.

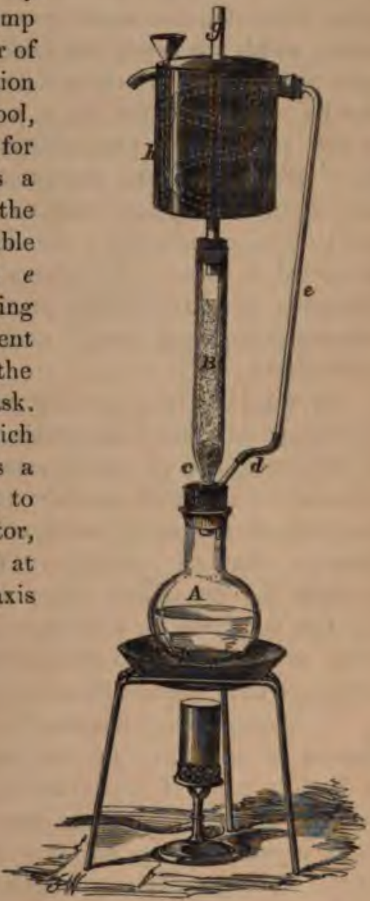
([illegible]) *Proximate Analysis.*—In the analysis of organic compounds, two problems are presented to the chemist for solution:—the object of the first is to separate the proximate components of the vegetable or animal product from each other; whilst the object of the second is to determine the elementary composition of the proximate principles thus isolated. The separation of wheat flour into starch, sugar, gluten, ligneous fibre, and oily matter, affords an instance of *proximate* analysis; but the determination of the proportions in which the carbon, hydrogen, and oxygen are united in the component starch, sugar, or fibre, furnishes an illustration of what is meant by *ultimate* organic analysis.

FIG. 352.



The proximate analysis of an organic compound is often a matter of great difficulty. The first process generally consists in the complete desiccation of a given weight of the substance under examination, by exposing it to a temperature of from 212° to 250° in a *water oven* or box of sheet copper, made double, as shown in fig. 352; *a* being an aperture for the introduction of oil or of water into the interval between the external and internal plates, the temperature being regulated by a thermometer introduced at *b*. The loss of weight which the substance under examination experiences during the drying can be accurately ascertained when needed. The dried material is then pulverized, and subjected to the action of several solvents in succession, such as ether, alcohol, and water. A convenient apparatus for the digestion of the substances for analysis in these menstrua, is shown in fig. 353:—A is a glass flask containing the liquid to be employed as the solvent: this can be kept in steady ebullition by means of the lamp beneath. B, is a tube of glass or of tin-plate, in the contracted portion of which is a plug of cotton wool, c; in this tube the substance for analysis is to be placed; *d*, is a short lateral tube to which the tube, *e*, of glass or of flexible metal is attached. The tube *e* should be kept warm, by enveloping it in flannel, with a view to prevent the premature condensation of the vapour which rises from the flask. M is a tin-plate condenser, which can be filled with water; *h*, is a funnel for conveying cold water to the bottom of this refrigerator, whilst the hot water flows off at the spout above; through the axis of M passes a tube, *g*, open at both ends; the lower projecting extremity of this tube is fitted by a cork to the top of the tube B. *f* is a worm tube, the upper extremity of which passes through the side of the refrigerator, and is adapted by a cork to the tube *e*, whilst its lower extremity is soldered to the tube *g*, into which its contents flow after they have been condensed in their passage through the refrigerator. It is obvious that by this arrangement a perpetual distillation of the liquid in the flask A, may be readily maintained; the vapour which passes through the tube *e*, becomes condensed in the spiral tube *f*, and percolates, in the liquid form, through the material contained in B, carrying the soluble matters into the flask A, where they

Fig. 353.



gradually accumulate. If the employment of metal be in any case objectionable, glass vessels may be used, but they are more fragile and more costly than those made of metal.

Ether is particularly valuable as a solvent for fatty substances, and for caoutchouc and camphor; alcohol, for the solution of many crystallizable organic principles, such as the vegetable alkalies; whilst water dissolves sugar, gum, starch, and other highly oxidized bodies, which are nearly insoluble in alcohol and in ether. In some cases benzol, in others chloroform, is a valuable solvent, and may be substituted for ether, which they most resemble in their solvent action. In particular cases dilute acids, and in others dilute alkalies may be employed, but they must be used with caution, since they are liable to act not merely as solvents, but also to produce important chemical changes upon the compounds submitted to them. No general rule can be laid down for the extraction of the different proximate principles; each class of substances requiring special modifications, which experience alone can indicate.

In all cases of proximate analysis, the employment of the microscope will afford invaluable aid whilst watching the progress of the separation of the various principles, and in enabling the operator to ascertain whether or not the substances which he has isolated are mixed with other bodies which may resemble them in chemical habitudes. When a substance or a deposit assumes the crystalline state, such an examination, by revealing the similarity or difference in form of its component particles, is often more valuable for ascertaining the purity of a substance than the use of ordinary chemical reagents.

It frequently happens that two or more substances, of different degrees of solubility in the same menstruum, occur together; in such a case, if crystallizable, they may often be separated by repeated crystallizations, care being taken always to separate those crystals which are first deposited from those which are formed subsequently: by successive recrystallizations of the first portions from each crop, the least soluble compound may be obtained in a state of purity. In other cases, if the different compounds yield precipitates with the same reagent, but differ in the degree of their affinity for it, a separation may be effected by adding a quantity of the precipitant insufficient to throw down, for example, more than one-half of the amount of the substances that may be present. The salts of silver or of lead may thus be added to mixtures of various organic acids, particularly to such as, like the fatty or the resinous acids, greatly resemble each other in properties. The precipitate is then suspended in water, and decomposed by means of sulphuretted hydrogen, or a dilute mineral acid, in order to separate the metal, and liberate the acid, which is again submitted to a similar incomplete precipitation; and this process is repeated until the fusing point becomes constant, or till some other guarantee of the purity of the body is obtained.

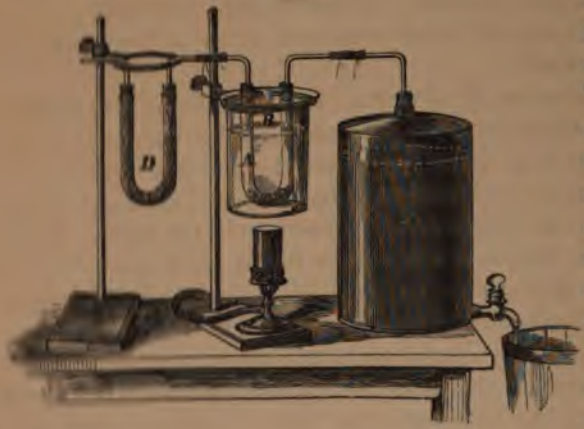
In the rectification of mixtures of volatile liquids, analogous principles are acted upon; in these cases the boiling point is the guide. The liquid is placed in a retort, into the tubulure of which a thermometer is fitted, and the temperature is raised till the liquid boils. So long as the temperature of the boiling liquid continues to rise, the substance which distils must consist of a mixture; but as soon as the point of ebullition becomes nearly stationary, the distillate may be supposed to have a composition nearly uniform; and by rectifying again those portions which distil at the same fixed temperatures, the different components of a mixed liquid may be obtained in a state of purity. This process of *fractional* distillation is well adapted to the separation of liquids, the boiling points of which differ considerably from each other; but it is much less satisfactory when they are within 20° or 30° of each other.

Liebig has applied a modification of this method to the separation of certain volatile acids from each other; and it may be employed generally in such cases with advantage. This process consists in saturating a portion of the acid liquid with potash or with soda, and then proceeding with the distillation; the more volatile acid passes over with the distillate. Suppose that it be desired to effect the separation of butyric from valeric acid:—a certain amount of potash is added, and if this be more than sufficient to saturate the valeric acid, the distillate will consist of butyric acid only, while the residue will be a mixture of valerate and butyrate of potash. If, on the other hand, the valeric acid be more than sufficient to saturate the potash, the residue in the retort will consist of pure valerate of potash, and the distillate will be a mixture of butyric and valeric acids, which may be separated by a repetition of the same process.

(901) *Ultimate Analysis.*—Before proceeding to the ultimate analysis of a body, it is necessary first to dry it carefully, either in the water oven (900), or by means of an apparatus similar to that shown in fig. 354, in which A represents a bent glass tube, for the reception of the substance to be dried; B, is a vessel of glass or of metal, containing water, or some saline solution; C, an aspi-

rator, by which a current of atmospheric air can be maintained through the apparatus; and D, a bent tube filled with fragments of pumice-stone, soaked in oil of vitriol, for drying in the air as it enters. The desiccation must be continued so long as the tube A ceases to lose weight. If the desiccation be effected in the water oven, the capsule or crucible which contains the compound must be allowed to cool under a bell glass, over a dish of oil of vitriol, and must be kept covered whilst being weighed, in order to prevent the absorption of moisture.

FIG. 354.



(902) *Determination of the Mineral Components.*—If any mineral substances be present in the compound under examination, the amount of these must be ascertained by the incineration of a weighed quantity of the material. This operation, simple as it may appear, is one, the exact performance of which is attended with considerable difficulty, which arises from the partial volatilization of the alkaline chlorides at a red heat, and the reduction of the sulphates to the form of sulphides. The incineration should, therefore, always be performed at a low temperature, which need not exceed a barely visible red, but must be prolonged for many hours if the mass for incineration be considerable. Caillat finds it advantageous in a large number of cases, before incinerating, to treat the substance with dilute nitric acid, by which means almost the entire saline ingredients may be extracted in the soluble form; on incinerating the insoluble portion, scarcely anything is left except silica and a small quantity of peroxide of iron. The quantity of saline matters thus obtained always exceeds that furnished by the former method; since in the digestion with nitric acid the loss occasioned by reduction of the sulphate of lime, and the partial expulsion of sulphur from the sulphide of calcium so formed, is avoided; the proportion of sulphuric acid

obtained is therefore always higher when nitric acid is used as a preliminary to incineration than when simple incineration is practised.

(903) Since the four elements, carbon, hydrogen, oxygen, and nitrogen, constitute the bulk of most organic substances, the operation of organic analysis resolves itself mainly into the accurate quantitative determination of these elements. We are indebted to Gay Lussac and Thénard for the fundamental principle that regulates our operations in this respect. The process proposed by them has subsequently been modified and improved by many chemists, especially by Berzelius, Prout, and Liebig, and it was by the last named eminent philosopher that the method now in general use was contrived.

The object of this operation being to determine the relative proportion in which each of the ultimate elements exists, it becomes necessary to the success of any analytical process that these elements should be procured either separately in a state of purity, or in the form of definite compounds that can easily be collected. In practice it has been found most convenient to supply the substance to be analysed with a quantity of oxygen sufficient to convert the carbon which it contains into carbonic acid, and the hydrogen into water; arrangements having been made for absorbing the carbonic acid by means of a known weight of a solution of potash; whilst the water, by passing it over a substance that has a powerful attraction for it, such as chloride of calcium or pumice moistened with sulphuric acid, is collected and weighed; the nitrogen is collected and measured in the form of gas, over mercury.

In certain cases where nitrogen is present, the substance to be analysed may be mixed with hydrate of soda or of potash, and heated; all the nitrogen is thus converted into ammonia, in which form, like carbonic acid, and water, it admits of being weighed. It is easy to find by calculation the weight of the carbon, the hydrogen, and the nitrogen respectively contained in the carbonic acid, the water, and the ammonia collected. When the proportion of saline matter has been determined by incineration of a portion of the mass, the quantity of oxygen which the substance contains may be known by deducting the united weight of the carbon, the hydrogen, the nitrogen, and the salts, from the total weight of the body analysed; the deficiency (supposing sulphur and phosphorus not to have been present) is reckoned as oxygen.

Scrupulous attention to the purity of the matter submitted to analysis is of course of primary importance, a very slight admixnate with other compounds being sufficient to vitiate the conclusions deducible from the experiments. Having by suitable means ascertained the purity of the substance to be analysed, the next care is to ensure its complete desiccation. Solids should be dried in the water oven (900). Volatile liquids that are unchanged by distillation should be allowed to stand for two or three days upon fragments of fused chloride of calcium; the liquid should then be decanted and distilled in a small retort. In other cases, as in the examination of fats or fixed oils, it may be more convenient to dry the material in a watch-glass placed in an ordinary water-bath, or in the hot-water oven. The further progress of the analysis will vary according to the form and composition of the substance to be examined.

We shall describe the methods of analysing—

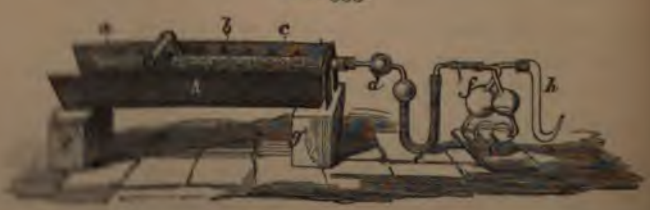
1. A *solid*, which does not contain nitrogen.
2. A *liquid*, which does not contain nitrogen.
3. A substance, which does contain nitrogen.

1. *Analysis of a Solid not containing Nitrogen.*

(904) The combustible which is generally used in these experiments is charcoal; it is very manageable, but the dust occasioned by it is troublesome. Hofmann has lately contrived a furnace in which gas is made use of as a fuel, and which answers the purpose admirably. (*Q. J. Chem. Soc.*, xi. 33.)

The best form of furnace to be used with charcoal is represented at A, fig. 355: it is made of stout sheet-iron bent into the

Fig. 355.



form of a trough, open at one end; the plate which closes th other end is perforated with an aperture three-quarters of an inc in diameter, to allow the passage of the combustion tube; th furnace is about 20 inches long, 5 inches wide at top, 2¼ inches bottom, and 3 inches high. Transverse slits are made along th floor at intervals of 2 inches for the admission of air, and betwee each of these slits are riveted vertical stiff pieces of sheet iro

1 inch high, terminating in a concave edge above, for the support of the combustion tube. During the operation, the apparatus may rest on bricks, *g*, *g*.

The tube in which the mixture is burned, the *combustion* or *retort tube*, (*a*, *b*, *c*,) should be about 15 inches long and half an inch in diameter, made of glass of difficult fusibility and free from lead: the hard Bohemian glass answers the purpose perfectly. The tube may on certain occasions be drawn out into a fine but strong tail bent upwards at an obtuse angle, and the mouth should be smoothed by making it red-hot in the flame of the blowpipe, so that a cork need not be torn in adjusting it.

The water is collected in a bent tube, *e*, filled with chloride of calcium. At *d* is a small bulb, in which the greater part of the water is condensed; it may be emptied from time to time. The chloride of calcium with which the bent portion is filled must not be fused, but should be prepared merely by evaporating the solution of the chloride to dryness by a strong sand heat. A porous mass is thus obtained, which does not expand by absorbing moisture, as the fused variety does, to the destruction of the tube that contains it. The 'cork through which passes the bent tube by which it is connected with the potash bulbs, *f*, should be trimmed close to the large tube and covered neatly with melted sealing-wax; and lastly, air should be drawn through the apparatus by the mouth to ascertain that no obstruction exists. Pumice-stone moistened with concentrated sulphuric acid may be advantageously substituted for chloride of calcium in the drying tube.

The connexion between this tube and the retort, *a*, *b*, *c*, is effected by means of a sound elastic cork, which is made to close the mouth of the tube accurately; it is pierced with a round file, and fitted firmly upon the fine tube proceeding from the bulb *d* of the drying tube; the cork is dried on the sand-bath immediately before the apparatus is mounted.

The solution of potash employed in the bulb tube *f*, should have a sp. gr. of from 1·25 to 1·27, and must be renewed for every experiment; the portions that have been used may be put aside, and afterwards, when sufficient has been collected, may again be rendered caustic in the usual way by means of quicklime. To the free end of the potash bulbs, a tube *h*, filled with fragments of hydrate of potash, is adjusted by means of a cork; this is weighed with the bulbs, and is employed to dry the nitrogen and other gases which escape during the course of the analysis.

The compound commonly used for supplying oxygen to the substance to be burned is oxide of copper; this oxide readily imparts oxygen to combustible matter which is in contact with it, but when heated alone, it bears a very high temperature without being decomposed. It is best procured by dissolving copper in pure nitric acid, evaporating to dryness and decomposing the nitrate by heating it strongly in an earthen crucible. Ignition is to be kept up till red fumes cease to appear; if the heat be too great the oxide becomes agglutinated, and requires strong pounding in an iron mortar to pulverize it. The powdered oxide is afterwards sifted through a fine copper sieve, and secured in stoppered glass bottles.

Immediately before each analytical operation, a sufficient quantity of this oxide is to be ignited in a crucible, and while still hot, transferred to a dry tube, by plunging the mouth of the tube into the oxide in the crucible, and then shaking it in piecemeal: the tube is to be immediately closed with a dry cork, and allowed to cool. Meantime the interior of the retort is to be completely dried by heating each portion of it in succession in the flame of a gas or spirit-lamp, beginning at the closed end, and drawing air through the heated tube by means of a narrower tube passed down just beyond the heated part, and exhausting by the mouth. When every part has thus been dried, the retort is to be corked and allowed to cool.

Five or six grains of the substance to be analysed, powdered and dried, are to be put into a perfectly dry test tube, and this tube with its contents very accurately weighed; its contents are then to be mixed with oxide of copper in a mortar, and the empty tube again weighed; the difference gives the weight of the substance employed. Much caution is requisite in charging the retort. The mortar having been first made dry and warm, is to be placed on a sheet of glazed paper, and cleared out with a little of the dried oxide of copper, which is thrown aside. Oxide of copper to the depth of an inch is to be poured into the combustion tube; after which a small quantity of the oxide is to be put into the mortar, then the substance to be analysed, then more oxide: the mixture must be made quickly and carefully, adding so much oxide as shall be sufficient to fill a little more than half the retort tube the mortar is then to be taken in the palm of the left hand, and the mixture introduced, carefully picking it up piecemeal by the retort tube itself: fresh portions of oxide are to be rubbed in the morta to clear out the last traces of the mixture, and the retort is finall to be filled up with pure oxide of copper to within two inches the extremity.

The proportions of the mixture are represented in fig. 355: the portion from the tail of the tube to the letter *a* consists of pure oxide of copper, from *a* to *b* of the mixture, from *b* to *c* of the rinsings of the mortar, and from *c* to within an inch of the cork is pure oxide. The tube having been closed by a cork is to be struck smartly in a horizontal position on the table, so as to clear the tail-like prolongation, and to make an air-way above the oxide from end to end.

The drying tube *e* having been accurately weighed, is next to be fitted to the dry perforated cork, and connected by it air-tight to the retort tube, *a*, *b*, *c*; this is now to be placed in the furnace; the potash apparatus, *f*, also previously weighed, is to be attached to the drying tube by means of a connecting piece of caoutchouc, taking care that the largest bulb is on the arm connected with the drying tube; the potash apparatus should be slightly inclined by placing a cork under the end of the horizontal portion nearest the open extremity. Matters being thus arranged, the next process is to ascertain if the whole be tight, and for this purpose the air in the large bulb is to be gently heated so as to expel a few bubbles; if, on cooling, the liquid rise in the limb and maintain its elevation steadily for a few minutes, the combustion may safely be begun. Charcoal broken into pieces about the size of a walnut is to be ignited, and applied to the portion of the tube nearest the cork, where the pure oxide of copper lies: the action of the heat is limited by a double sheet-iron screen which fits into the furnace, and has a central slit in order to allow it to bestride the tube; this screen can by degrees be moved further and further down the furnace until the whole tube is heated. An additional screen of single iron plate is hung over the closed end of the furnace to protect the cork, care being taken that the heat never rises so high as to scorch it, or falls so low as to allow of the condensation of moisture in the portion of the retort which projects from the furnace.

When the fore part of the retort is red-hot and the escape of air due to expansion has ceased, about an inch more of it may be heated; and in this way the fire is gradually carried down. At first but a small portion of the gas is absorbed, but when the substance is fairly undergoing decomposition, and the atmospheric air in the apparatus has been expelled, the gas is almost entirely taken up by the potash-ley. When the whole tube is ignited, the heat must be continued till bubbles are no longer disengaged; the potash-ley will now gradually recede into the large bulb; when this is observed to commence, the charcoal must be removed from the tail of the tube; and as soon as the solution of potash has risen sufficiently to fill half the large bulb, the tip of the tail must be nipped off; gentle suction is then to be effected by means of a tube of vulcanized caoutchouc, which is to be fitted to the free extremity of the potash apparatus, and air drawn through the combustion tube by the mouth, in order to displace the carbonic acid and aqueous vapour which the apparatus contains. Dumas prefers to connect the extremity of the retort with a drying tube, and this again with a receiver containing oxygen, which gas is carefully driven over the contents of the tube in the manner shown in fig. 265, part ii., p. 72. This renders the operation somewhat more complicated, but it is unquestionably more exact, especially for compounds where the proportion of carbon is great. The tube for supplying oxygen is easily adjusted to the retort by drawing out the tail horizontally instead of obliquely, and fitting it on by a caoutchouc connector, care being taken to screen the junction from the influence of heat.

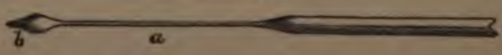
The apparatus is now to be dismounted, and allowed to cool: in about an hour the drying tube *e* may be weighed; one-ninth of the gain which it has experienced indicates the quantity of hydrogen contained in the compound analysed; the potash apparatus, *f*, is also to be weighed, and three-elevenths of what it has gained shows the quantity of carbon. The deficiency is reckoned as oxygen.

The oxide of copper used in these experiments may again be rendered serviceable by moistening it with nitric acid, and igniting it as before.

2. *Analysis of a Liquid not containing Nitrogen.*

(905) If the liquid be *volatile*, a piece of tube rather less than a quarter of an inch in diameter is to be heated in the blowpipe flame, and drawn out into a capillary portion, *a*, (fig. 356,) about four inches long: about a quarter of an inch below this the tube

FIG. 356.



is to be sealed, and the little piece of tube, *b*, thus left connected with the capillary part, heated and blown into a small bulb about as big as a good-sized pea; this is to be cut off, leaving a capillary neck of about two inches long. Having made a sufficient number of these small bulbs, two of them, which it has been ascertained will freely enter the combustion-tube, are to be accurately weighed a little of the liquid to be analysed is to be put into a small tube, and the capillary neck of the bulbs inverted into the liquid; the bulbs are then to be warmed by the flame of a spirit-lamp, so that on cooling they shall be about three-fourths filled with the liquid. The necks are now to be sealed by the blowpipe-flame, and the bulbs again weighed; the increase of weight gives the quantity of the liquid which has entered, and which is to be analysed. The oxide of copper having been heated, and allowed to cool with the usual precautions, about an inch and a half of the retort is to be filled with pure oxide; next a file is to be drawn across the capillary neck of one of the bulbs, and the bulb having been placed in the retort, the neck is to be broken by pressure against the glass, and the broken portion of the neck to be dropped in with the bulb; dried oxide of copper is then to be poured in to the depth of two inches more; the second bulb is to be introduced in the same manner as the first, and the tube is to be filled up with oxide; after which it is to be corked and struck smartly upon its side on the table, to secure free air-way. The combustion tube is now to be adjusted in the furnace, and the first half of the tube is to be gradually heated; when this is red-hot, the liquid must be volatilized by cautiously approximating a piece of ignited charcoal to the part of the tube where the bulb nearest the open end of the retort lies, taking especial care not to raise the temperature too rapidly: when by degrees all the liquid in the first bulb has been expelled, the other is to be proceeded with in like manner; the whole tube is finally to be heated carefully, and the gases are to be swept out of the apparatus in the manner already described.

Substances which contain a great excess of carbon sometimes escape complete combustion by the above process; when this is feared, the tube is connected with a receiver filled with oxygen, upon the plan of Dumas, already mentioned; or some finely pulverized, carefully dried chlorate of potash may be mixed with about four times its weight of oxide of copper, and the portion of the retort near *a* (fig. 355) may be filled with it for about an inch; the tail-like prolongation may in this case be dispensed with: at the close of the operation, instead of sucking air through the apparatus, heat is to be very cautiously applied to the chlorate; by this means oxygen is evolved; this burns the last traces of carbon and displaces the gas and aqueous vapour contained in the tubes. The heat must not be too suddenly applied, for if it be, a portion of the chlorate is apt to be carried forward mechanically, a circumstance which constitutes the chief objection to its use.

In some cases *chromate of lead* may be advantageously substituted for oxide of copper with substances difficult of combustion, since by a bright red heat alone it gives off a portion of its oxygen. It is easily prepared by precipitating the chromate or bichromate of potash with a solution of acetate of lead: it should be well washed and heated to incipient fusion before it is used for analysis. Chromate of lead has the advantage of being much less hygroscopic than the oxide of copper. In some cases it may be mixed with bichromate of potash, which parts with oxygen by heat more freely than the lead salt.

3. *Analysis of a Body containing Nitrogen.*

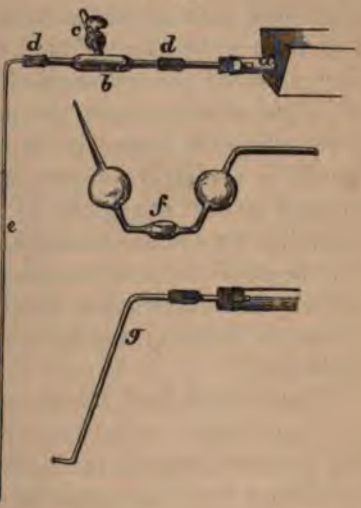
(906) The presence of nitrogen in an organic compound is ascertained by mixing a small quantity of it with a portion of hydrate of potash, and heating it in a small test tube: vapours of ammonia will be evolved if nitrogen be present. Two separate analyses are in this case required; the first, to discover the proportion of carbon and hydrogen; and the second, expressly for the nitrogen. When bodies containing nitrogen are burned with oxide of copper, a variable proportion of the lower oxides of nitrogen is formed, which being retained by the chloride of calcium, or by the potash, would render the analysis incorrect. A precaution is therefore employed which renders it necessary to make use of a retort-tube somewhat longer than common; this tube is to be charged as usual to within 4 inches of the opening, and then filled up with clean copper turnings; the apparatus is to be arranged as before directed, the copper turnings brought to full redness, and the analysis is to be cautiously conducted in the ordinary manner. As the oxides of nitrogen pass slowly over the ignited copper they are decomposed, the oxygen combining with the copper, while pure nitrogen escapes: the quantity of carbon and hydrogen is determined exactly in the manner previously described.

(907) *Method of Varrentrapp and Will.*—The most accurate method for ascertaining the proportion of nitrogen is that devised by Varrentrapp and Will; the fundamental fact upon which this method is based, consists in the observation of Gay Lussac, that when azotised matters are heated with a large excess of hydrate of potash or of soda, the whole of the nitrogen is expelled in the form of ammonia. In order to render i available for the purposes of analysis, the subjoined precaution are requisite.

A mixture of two parts of quicklime and one of hydrate of oda is prepared by slaking some well-burned lime with the necesary quantity of a solution of soda; the whole is evaporated to ryness and ignited; the dry mass is pulverized as quickly as ossible, and then transferred to well-closed bottles, in order to xclude carbonic acid and moisture. When an analysis is reuired, the substance under examination is very intimately mixed n a warm mortar with a portion of this alkalized lime, or *sodaime* as it is frequently termed, instead of with oxide of copper: he accidental presence of a little moisture, after the weight of the naterial for analysis has been accurately determined, is of no onsequence in this case.

Having introduced the mixture into the retort tube, it is etter to plug the aperture loosely with a few fibres of asbestos (which has been ignited just efore) to prevent any mechaical transport of the mixture nto the apparatus through which the gases are made to ass; on applying heat to the combustion-tube in the ordinary way, and with the usual precautions, the substance is decomosed, and the whole of the itrogen escapes as ammonia. The drying tube and potash pparatus are dispensed with, nd the ammonia is collected in a bulb-tube of the form represented at *f*, fig. 357, which is onnected, air tight, by means of a good cork, with the retorttube, *a*; the bulbs *f* having been reviously charged with hydrochloric acid of sp. gr. 1·1.

FIG. 357.



Pure hydrochloric acid is easily procured for this purpose by iluting the ordinary acid of the shops till it has a sp. gr. of 1·1, and distilling it in glass vessels; the first eighth may be rejected, and the distillation proceeded with until three-fourths of the acid mployed have passed over. It is better for the operator always to rectify his own acid, in order to be quite sure of the absence of any trace of ammonia.

The tube connecting the bulbs *f* should be somewhat larger n diameter than that of the ordinary potash apparatus, in order to allow the liquid to be poured out readily. When the operation is complete, absorption will take place, and the liquid will rise in the bulb nearest the fire; at this moment the tail of the combustion-tube should be nipped off, and air carefully drawn through the apparatus in the usual way. When the combustion is completed, the contents of the bulb-tube are to be emptied into a small evaporating dish, and the bulbs washed out first with a mixture of alcohol and ether, and afterwards several times with water; some solution of bichloride of platinum is to be added, and the whole evaporated to dryness in a water-bath or a chloride of calcium bath; the residue when dry is to be digested with a mixture of two parts of alcohol, sp. gr. 0·833, and one of ether, which dissolves the excess of bichloride of platinum, and leaves the double chloride of platinum and ammonium in a crystalline form. This must now be brought upon a weighed filter, and washed repeatedly with the mixture of two parts of alcohol and one of ether until nothing further is taken up; the precipitate and filter must be dried by a heat of 212°, and the weight accurately observed: 220·52 grs. of the ammonia-chloride of platinum are equivalent to 14 grs. of nitrogen, or 100 parts to 6·348 of nitrogen. Instead of collecting the ammonia in hydrochloric acid, it may be condensed in a certain volume of dilute sulphuric acid of known strength (about 150 grains of an acid of which 100 grains will neutralize 2·5 grains of ammonia, will answer the purpose). The acid liquor is then to be washed out of the bulbs *f*, diluted, and carefully neutralized by a solution of caustic soda, or by a solution of lime in dilute syrup, the strength of which has been accurately graduated.

(908) *Method of Dumas.*—The foregoing method of determining nitrogen answers for nearly all cases excepting those in which this element occurs in the form of nitric acid, when it must be determined by volume, and its weight thence deduced. For this purpose the process of Dumas is the most trustworthy:—A retort tube of about 20 inches long is employed, not drawn out into a tail, but sealed with a rounded extremity; about 2 inches of the tube are filled with bicarbonate of soda, and then the mixture with oxide of copper is added, and covered as usual with a layer of pure oxide; beyond this, the last 2 or 3 inches of the tube are filled with clean copper turnings, as already directed, with a view of decomposing any of the oxides of nitrogen which may be formed. The retort tube is then connected with a three-legged apparatus of brass or copper (fig. 357, *b*), one limb of which is furnished with a stopcock, *c*. The connexion with the retort tube *a* is best

made by passing a piece of glass tubing through a cork fitting accurately into the mouth of the tube *a*, and connecting the brass apparatus to this small glass tube by a caoutchouc connector, *d*; the third limb is fastened by a similar joint to a glass tube *e*, bent at right angles near one end, with a straight portion upwards of 30 inches long, the other extremity of which is turned up at an acute angle for the convenience of safely delivering the gas: this tube is placed with its long portion in a vertical direction and with its lower upturned extremity dipping into a small mercurial trough; the stopcock tube, *c*, is connected with an exhausting syringe, by which a vacuum is produced; the apparatus is left for half an hour to ascertain that all the joints are tight: if the mercury after this lapse of time still stands at the same level, the experiment may be proceeded with. A moderate heat is then applied by a spirit lamp at the end of the retort containing the bicarbonate; by this means carbonic acid is set free and displaces the last portions of air; the exhaustion and the disengagement of gas are repeated alternately three or four times, care being taken to leave an amount of the bicarbonate undecomposed sufficient to renew this expulsive process at the termination of the experiment. The stopcock, *c*, is now closed, the air-pump is removed, and a graduated jar containing some solution of potash is inverted in the mercury over the recurved extremity of the long glass tube. The copper turnings are then brought to redness in the usual way by means of a charcoal fire, the decomposition being caused to take place less rapidly than usual. When the part of the retort containing the matter for analysis is red-hot through its entire extent, heat is gradually applied to the bicarbonate of soda, and the last portions of gas furnished by the combustion are driven into the receiver by the carbonic acid disengaged from the bicarbonate.

The products of the combustion are only water, carbonic acid, and nitrogen; the former two are retained by the solution of potash, whilst the nitrogen alone presents itself for measurement. When the apparatus by standing for an hour or two has reached the temperature of the atmosphere, the height of the barometer and thermometer must be carefully noticed; and since the gas will be saturated with moisture, its volume must be corrected by the known methods for the three points of temperature, pressure, and moisture: then, since 100 cubic inches of nitrogen at 60° F. and under a pressure of 30 inches of mercury weigh 30·15 grains, it is easy to calculate the weight of the nitrogen that is contained in a given quantity of the matter analysed. In this process, as in every case where the proportion of nitrogen alone forms the object of the experiment, after the weight of the material for analysis has been once accurately ascertained, it is evident that there is nothing to fear from a slight absorption of moisture.

(909) *Method of Relative Volumes.*—When the quantity of nitrogen present is not less than one-fourth of the weight of the carbon contained in the compound, its proportion may be advantageously determined by making the combustion just as though we were going to ascertain the proportion of carbon and hydrogen; but, instead of condensing the carbonic acid and weighing it, the whole of the gases produced are collected over mercury. A bent gas-delivering tube *g*, fig. 357, is substituted for the usual apparatus, for the absorption of water and carbonic acid. In this case it is best to begin at the closed extremity of the tube, and having expelled the atmospheric air by a portion of gas generated from the substance, to collect the rest of the gaseous products in a graduated jar; by agitating the gas with a solution of potash, the proportion of nitrogen to the carbon is at once determined, since equal volumes of carbonic acid and nitrogen gases represent single atoms of carbon and nitrogen. It is not necessary in this case to weigh accurately the quantity of material acted upon.

Experience has shown that in the preceding process for organic analysis, the quantity of hydrogen deduced from it is always slightly in excess, usually about 0·2 parts in 100, whilst, unless chromate of lead or chlorate of potash be employed, the carbon is sometimes deficient to the same extent. A deficiency of carbon also occurs if the ash contain carbonates of the alkalies or of the earths.

(910) *Determination of Sulphur and of Phosphorus.*—One of the methods employed for ascertaining the amount of unoxidized sulphur in an organic compound, consists in mixing 1 part of the substance for analysis with 10 parts of nitre, 2 of dried carbonate of soda, and 30 of pure chloride of sodium, and heating the mass to redness in a tube of hard glass. The sulphur is thus converted into sulphuric acid, which enters into combination with a portion of the alkali. The object of adding the chloride of sodium is simply to moderate the violence of the deflagration. The residue is to be dissolved in water rendered slightly acid with hydrochloric acid, and the sulphuric acid precipitated by the addition of chloride of barium. If phosphorus be present, it will remain in the acid liquor in the form of phosphoric acid. Its amount may be determined by adding sulphuric acid to throw down the excess of baryta, filtering, supersaturating with ammonia, and adding an

ammoniacal solution of sulphate of magnesia; the phosphoric acid is precipitated as the double phosphate of magnesia and ammonia, and is to be collected and ignited in the usual manner.

When a large quantity of sulphur is present, an error might easily occur in the estimation of the amount of carbon, since a portion of the sulphur becomes converted during the process of combustion with oxide of copper into sulphurous acid, and this would be condensed by the potash along with the carbonic acid, which would thus be estimated in excess. This source of error may be avoided by interposing a short tube filled with peroxide of lead between the tube of chloride of calcium and the potash bulbs; the sulphurous acid is then arrested and converted into sulphuric acid, and is retained as sulphate of lead; $2PbO_2 + S_2O_4$ becoming $2\,PbO,S_2O_6$.

(911) *Determination of Chlorine, Bromine, and Iodine.*—When the quantity of chlorine, or of any other halogen, is to be estimated, the substance for analysis is to be mingled with about 10 times its weight of lime, and introduced into a tube of Bohemian glass 10 or 12 inches long, and sealed at one end. The tube is to be filled up with fragments of pure lime, which is gradually brought to a red heat, commencing at the open extremity. When the combustion is complete, the tube is corked, its outer surface cleared from ashes, and whilst still hot it is plunged into a beaker of cold water. It is thus cracked, and its contents are then treated with nitric acid, and the chlorine, iodine, or bromine is precipitated from the filtered liquid by means of nitrate of silver.

(912) *Calculation of the Combining Proportion of an Organic Body.*—We will suppose the labour of analysis thus brought to a successful issue. It is evident that the information derived from this source alone is but scanty, for it furnishes no idea either of the number of atoms of each element entering into the molecule of the organic body, or of the relations of the body to the substances concerned in its production or obtainable from it by its decomposition. Whenever it is possible, the equivalent or combining proportion of the compound must be determined. This is effected by preparing a compound of the body with some substance the combining proportion of which is well known, and proceeding to analyse the new product. If the organic substance be soluble in water, and capable of entering into combination with oxide of silver, this oxide is for many reasons to be preferred. Oxide of silver combines with many organic bodies, and forms with them compounds insoluble or but sparingly soluble in water; and they may generally be formed by double decomposition, and washed

from all adhering impurities. Supposing a silver compound have been prepared in a state of purity, 15 or 20 grains of it a to be accurately weighed in a counterpoised porcelain crucib It is then to be carefully incinerated till pure silver alo remains. On again weighing, the loss will give that of the bo combined with the silver, and in addition that of one equivale of oxygen expelled from the oxide of that metal at red heat. T residual silver should be soluble without remainder in nitric ac From the weight of the metallic silver, the combining number of t organic body that had combined with it may be readily calculat

An example will best explain the method of proceeding:—

48·73 grs. of acetate of silver left
31·49 grs. of metallic silver.

17·24 will therefore express the loss, due to the united weig of acetic acid and oxygen combined with silver; then,

$31{\cdot}49 : \left\{\overset{\text{at. wt. silver.}}{108}\right. :: 17{\cdot}24 : x\ (=59)$; and

$59 - \left\{\overset{\text{at. wt. oxygen.}}{8}\right. = 51$, the combining number of acetic acid.

Another example will show the method of calculating the nu ber of atoms of each element in an equivalent of the compound

By combustion with oxide of copper it is found that 10 grs. acetate of silver yield

		Grains.	
5·277 grains of carbonic acid	=	1·439	carbon
1·620 grains of water . .	=	0·180	hydrogen
And (from previous expt.) .		6·462	silver
The deficiency	=	1·919	oxygen.
		10·000	

Then by proportion—

$\overset{\text{Silver.}}{6{\cdot}462} : \overset{\text{at. wt. silver.}}{108} :: \left\{\overset{\text{Carbon.}}{1{\cdot}439}\right. : x\ (=24)$, or C_4.

$6{\cdot}462 : 108 :: \left\{\overset{\text{Hydrogen.}}{0{\cdot}180}\right. : y\ (=\ 3)$, or H_3.

$6{\cdot}462 : 108 :: \left\{\overset{\text{Oxygen.}}{1{\cdot}919}\right. : z\ (=32)$, or O_4.

Total . . . . . . =59
deduct 1 equivalent of oxygen . . . 8

and we obtain the combining number of anhydrous acetic acid . . . } 51, or C_4H_3O

In some cases the required compound with silver cannot obtained: a salt of lead is then, if practicable, substituted fo

The residue after incineration in this case does not consist entirely of metallic lead, neither is it all oxide of lead. In order to determine the proportion of each, the residue is carefully weighed, and treated with acetic acid in the crucible itself; the oxide of lead is thus dissolved and washed away. When the contents of the crucible have been carefully dried, a second weighing gives the quantity of metallic lead, whilst the loss furnishes that of the oxide. From the metal the quantity of oxide to which it is equivalent may be calculated; this, added to the portion dissolved by acetic acid, furnishes the whole quantity of oxide contained in the compound: a calculation, similar to that employed for the silver salt, then supplies the equivalent number of the body analysed. The method is not quite so accurate as the preceding one; it involves more manipulation, and the compounds of lead are apt at a high temperature to undergo slight loss by volatilization.

Just as the combining number of an acid can be ascertained by determining the amount of any base with which it enters into combination, so may the combining number of a body possessed of marked basic properties—morphia or aniline, for example—be discovered by causing it to enter into combination with a well-defined acid such as the hydrochloric, and ascertaining the amount of such acid with which a given weight of the base will unite. The hydrochlorates of many bases form crystallizable double salts with bichloride of platinum; when this is the case, the double salt is frequently employed in the determination of the combining proportion of the organic base which it contains.

(913) *Relation of Vapour Density to Molecular Formulæ.*—In all cases where it is practicable, it is of great importance to ascertain the vapour density of the compound, since, if this be once known, it is easy to calculate the molecular formula of the compound, whilst from the molecular formula it is equally easy to calculate the vapour density of the body. In order to calculate the vapour density of any compound from its molecular formula, it is assumed, in accordance with the results of observation upon the compounds of carbon almost without exception, that the volume of the molecule of the body in the state of vapour is 4 times that of oxygen, (if $O=8$, and $H=1$), and consequently double that of hydrogen; or, that it corresponds to H_2; H_2 being, in fact, upon Gerhardt's view, the representative of the molecule of hydrogen when in the *free* state. Now, according to Regnault's experiments, the weight of a given bulk of atmospheric air is 14·47 times that of an equal bulk of hydrogen under similar circumstances of temperature and pressure: consequently, doubling this for H_2 (the molecule of free

hydrogen), we obtain $\frac{2}{2\times 14\cdot 47}=0\cdot 0691$ as the vapour density, or specific gravity, of hydrogen. And in like manner by dividing the molecular weight *m*, of any organic compound, by $2\times 14\cdot 47$ (or 28·94), we obtain the vapour density *d* of the compound; $\frac{m}{28\cdot 94}=d$.

For example, the molecular formula of Marsh gas is C_2H_4, and its *molecular weight*, or the sum of the atomic weights of its component elements, is 16. Now $\frac{16}{28\cdot 94}=0\cdot 55$, and this number agrees with Thomson's experimental determination of the density of the gas.

On the other hand, if the vapour density of a compound be known, and if its percentage composition have been determined, the accuracy of the molecular formula of the body may be checked by reversing the foregoing process; that is to say, by multiplying the vapour density by 28·94, we obtain a very close approximation to the molecular weight, since $d\times 28\cdot 94=m$. The numbers obtained by this calculation are never absolutely correct, owing to unavoidable experimental errors in ascertaining the vapour density; but the errors do not affect the value of the result in controlling the molecular formula; the atomic constitution of the molecule may be safely inferred from the calculated result; and thus the accuracy of the formula deduced from the analytical operations may be checked.

For example, the experimental determination of the specific gravity of the vapour of ether shows it to be 2·586. Now, $2\cdot 586\times 28\cdot 94=74\cdot 26$. The simplest formula deducible from the analysis of ether is C_4H_5O, corresponding with the molecular weight 37; but the foregoing calculation indicates that this formula must be doubled, in which case it becomes $(C_4H_5O)_2$, and the corresponding molecular weight (=74) agrees as closely as can be desired with the result of the calculation from the vapour density.

It would, however, be out of place here to enter further into the methods of checking the correctness of an analysis in its various parts. For information upon this point, the reader is referred to Liebig's *Handbook of Organic Analysis*. The subject is an important one, and it is not always sufficiently attended to by those who devote themselves to analytical researches of this description.

§ II.—Classification of Organic Compounds.

(914) *General Principles of Classification.*—The classification of the immense variety of compounds that are presented to the chemist, either naturally by the organs of the living vegetable or animal, or that are derivable from the bodies so obtained by the employment of chemical reagents, may be effected upon two prin-

ciples. The first of these, which rests upon analogies of function (according to which bodies are arranged under the head of acids, bases, &c.), might seem to be the more natural, but the second, which is based on the chemical relations of the different compounds, is the truly philosophical system. The first method of arrangement was the only practicable one in the infant state of the science, and it still presents certain advantages to the student in the early stage of his career; but the second will eventually supersede the former, as it greatly facilitates the important study of the true analogies of the different compounds with each other. The time is approaching when, to use the words of Gerhardt, "organic chemistry, awarding to physical characters and chemical functions but a secondary importance as means of classification, must rest upon some wider principle which is applicable to all substances, whatever may be their physical characters and their chemical functions. After having studied bodies in relation to the metamorphoses of which they are susceptible, *she must group together those which are derived one from the other*, and when she has thus arranged a certain number of groups, or of series, she must inquire whether amongst the bodies which these groups embrace, there be not some which have a higher degree of resemblance to each other than they have to the other combinations of the same group, and which consequently produce, in a manner more or less complete, combinations belonging to the same type. Passing, then, from the comparison of these different terms, to the comparison of the different groups taken collectively, she discovers new analogies, she finds recurring groups or parallel series; and from this parallelism she at length deduces some general formula which sums up the constitution and the metamorphoses of the entire collection of groups or of series."—*Traité de Chimie Organique*, i. 122.

Since, however, the true relations of a great number of bodies to each other have been as yet only imperfectly traced, the most devoted admirer of a strictly chemical classification is obliged to make a large appendix of unclassified bodies, and to bring into the more systematically arranged portion of his subject many substances which have but a questionable title to the place accorded to them; moreover, a rigid adherence to such a principle of classification would lead to the separation of bodies which in their applications and in general properties are closely allied. We shall, therefore, here, as in other portions of the present work, be guided rather by considerations of convenience than by the rigid requirements of system; and shall endeavour to select such a method of arrangement as shall most facilitate the progress of the student.

In the present work, the various compounds of organic chemistry will be examined in the following order :—

1. Sugar, starch, and ligneous fibre.
2. Alcohols, ethers, and their derivatives.
3. Fats, fixed oils, and their allied acids.
4. Certain organic acids of vegetable origin.
5. Amides and organic bases.
6. Essential oils and resins.
7. Colouring matters.
8. Products of destructive distillation.
9. Cyanogen and its derivatives.
10. Nitrogenized principles of plants and animals.
11. Certain products peculiar to animals.

(915) *Classification in Homologous Series.*—It will, however, be advantageous to illustrate more fully the principle of the chemical classification by means of a few examples. This purpose may be answered by examining the relations of alcohol or spirit of wine to other bodies which resemble it.

1. *Alcohols.*—Alcohol or spirit of wine is the most important member of a group of compounds which manifest a close analogy with each other, both in chemical composition and in the decompositions of which they are susceptible. In the following table the composition of most of the different bodies which may be classed under the generic term of alcohols is exhibited :—

	$(C_nH_{n+2})O_2$	Boiling Point °F.
Wood Spirit	$C_2H_4O_2$	149·9
Alcohol	$C_4H_6O_2$ or $C_2H_4O_2 + (C_2H_2)$	173·1
Tritylic or Propylic Alcohol	$C_6H_8O_2$ or $C_2H_4O_2 + 2\,(C_2H_2)$	205
Tetrylic or Butylic Alcohol	$C_8H_{10}O_2$ or $C_2H_4O_2 + 3\,(C_2H_2)$	226 (?)
Amylic Alcohol (fousel oil)	$C_{10}H_{12}O_2$ or $C_2H_4O_2 + 4\,(C_2H_2)$	269·8
Hexylic or Caproic Alcohol	$C_{12}H_{14}O_2$ or $C_2H_4O_2 + 5\,(C_2H_2)$	300 (?)
Octylic (caprylic) Alcohol .	$C_{16}H_{18}O_2$ or $C_2H_4O_2 + 7\,(C_2H_2)$	
Laurylic Alcohol	$C_{24}H_{26}O_2$ or $C_2H_4O_2 + 11\,(C_2H_2)$	
Cetylic Alcohol (Ethal) . .	$C_{32}H_{34}O_2$ or $C_2H_4O_2 + 15\,(C_2H_2)$	
Cerylic Alcohol.	$C_{54}H_{56}O_2$ or $C_2H_4O_2 + 26\,(C_2H_2)$	
Melissylic Alcohol. . . .	$C_{60}H_{62}O_2$ or $C_2H_4O_2 + 29\,(C_2H_2)$	

Now, on inspecting the formulæ of the alcohols contained in the foregoing table, it will be seen that each of the first six compounds contains a quantity of carbon and of hydrogen less by C_2H_2 than the compound immediately beneath it : so that each may be regarded as a compound analogous to wood spirit, but containing a certain additional number of multiples of the hydrocarbon C_2H_2. Bodies of analogous properties which stand thus related to each other, or which differ by a multiple of C_2H_2, are said to be *homologous*. Wood spirit and fousel oil, as well as ethal and cerylic alcohol, are termed *homologues* of wine alcohol. These different compounds may be represented under a common formula, viz., $(C_nH_{n+2}O_2)$, or $(HO,C_nH_{n+1}O)$, where *n* represents 2, 4, 6, or any even number. The boiling point of these homologous bodies, it will be observed, rises with each additional increment of C_2H_2 by about 33° F.

(916) *Classification in Heterologous or Collateral Series.*—This principle of classification admits of extension in other directions. Every compound in a homologous series when subjected to the action of chemical reagents furnishes other compounds, differing in composition from that from which they are obtained, but yet bearing a definite relation to it. Thus alcohol yields under various circumstances ether, aldehyd, acetic acid, &c.; and these *heterologous* or differently constituted bodies belong to collateral, and intimately related, but different series: for it is found that the different members of a homologous series exhibit an analogous deportment when submitted to similar chemical reagents, and furnish derivative series in which the homology is still preserved. We may exemplify the formation of these collateral series in the derivatives obtained from the alcohols.

2. *Vinic Acids.*—When ordinary alcohol is mixed with an equal weight of strong sulphuric acid, a large portion of the alcohol and of the acid decompose each other, water is formed, whilst a new compound acid termed sulphovinic or sulphethylic acid (HO, C_4H_5O,S_2O_6) is produced; one molecule $(2\ HO,S_2O_6)$ of sulphuric acid acting upon the elements of 1 molecule (C_4H_5O,HO) of alcohol, whilst water in the proportion of H_2O_2, is liberated. Now wood spirit, fousel oil, and each of the other alcohols, when similarly treated, furnishes a compound perfectly analogous to sulphethylic acid, as is represented in the following table:—

Sulphomethylic Acid	HO,C_2H_3O,S_2O_6
Sulphethylic (sulphovinic) Acid	HO,C_4H_5O,S_2O_6
Sulphotritylic Acid	HO,C_6H_7O,S_2O_6
Sulphotetrylic Acid	HO,C_8H_9O,S_2O_6
Sulphamylic Acid	$HO,C_{10}H_{11}O,S_2O_6$

the general formula for these vinic acids being $(HO,C_nH_{n+1}O, S_2O_6)$.

3. *Ethers.*—If sulphethylic acid, or if a mixture of equal volumes of sulphuric acid and alcohol, be exposed to heat in a retort and distilled, a volatile liquid which has been long known under the name of *ether* passes over; and a similar body may be obtained from the other alcohols. The composition of these different ethers

is such that all admit of being represented by formulæ which contain the same elements as the alcohols which yield them, minus water in the proportion of HO ; thus :—

	$C_nH_{n+1}O$		$(C_nH_{n+1}O)_2$
Methylic Ether	C_2H_3O	or	$(C_2H_3O)_2$
Vinic (or ordinary) Ether . .	C_4H_5O	or	$(C_4H_5O)_2$
Tritylic (propylic) Ether . .	C_6H_7O	or	$(C_6H_7O)_2$
Tetrylic (butylic) Ether . . .	C_8H_9O	or	$(C_8H_9O)_2$
Amylic Ether	$C_{10}H_{11}O$	or	$(C_{10}H_{11}O)_2$

the general formula for these ethers being $(C_nH_{n+1}O)$; consequently they may be regarded as being derived from one molecule of each alcohol by the abstraction of water in the proportion of HO ; for instance—

$$\overbrace{C_4H_5O,HO}^{\text{Alcohol.}} - HO = \overbrace{C_4H_5O,}^{\text{Ether.}}$$

or, generally, $(C_nH_{n+1}O,HO) - HO = C_nH_{n+1}O$. It is, however, more probable that they are formed not from 1 molecule, but, as will be shown hereafter (989), that they are derived from 2 molecules of alcohol, by the removal of water in the proportion of H_2O_2;

$$2\,(C_nH_{n+1}O,HO) - H_2O_2 = (C_nH_{n+1}O)_2.$$

4. *Hydrochloric and other corresponding Ethers.*—The ethers in their turn admit of the displacement of the oxygen which they contain, by chlorine, bromine, or iodine, and they thus produce a number of bodies analogous to each other;—if alcohol be treated with hydrochloric, hydrobromic, or hydriodic acid, instead of with sulphuric acid, water is separated, and chloride, bromide, or iodide of ethyl is formed ; for example :—$C_4H_6O_2 + HCl = C_4H_5Cl + H_2O_2$.

The following table exhibits the analogy and the homology of these compounds :—

Compounds.	Chloride.	Bromide.	Iodide.
Methyl.	C_2H_3Cl	C_2H_3Br	C_2H_3I
Ethyl	C_4H_5Cl	C_4H_5Br	C_4H_5I
Trityl (Propyl) . .	C_6H_7Cl		
Tetryl (Butyl) . .	C_8H_9Cl		
Amyl	$C_{10}H_{11}Cl$	$C_{10}H_{11}Br$	$C_{10}H_{11}I$

In the preceding table several blank spaces appear, the compounds corresponding to them not having been formed as yet, though there is no doubt that they could be obtained without difficulty.

5. *Hydrocarbon Radicles of the Ethers.*—When iodide of ethyl

is sealed up in a strong tube and heated to about 300°, in contact with metallic zinc, iodide of zinc and a quantity of a peculiar hydrocarbon $(C_4H_5)_2$ is set at liberty. This substance has been termed *ethyl*, and has been regarded as the basis of ether, which has the composition of an oxide of this hydrocarbon. By analogous means bodies corresponding in composition to the radicles of several of the other ethers have also been isolated. The general formula of these compounds may be represented as (C_nH_{n+1}), or rather, when isolated, as $(C_nH_{n+1})_2$;* thus—

Methyl	C_2H_3	or	$(C_2H_3)_2$
Ethyl	C_4H_5	or	$(C_4H_5)_2$
Trityl (Propyl)	C_6H_7	or	$(C_6H_7)_2$
Tetryl (Butyl)	C_8H_9	or	$(C_8H_9)_2$
Amyl	$C_{10}H_{11}$	or	$(C_{10}H_{11})_2$

6. *Homologous Hydrocarbons of the form* (C_nH_n).—If alcohol be treated with three or four times its volume of sulphuric acid, or with anhydrous phosphoric acid, and be distilled, each molecule of alcohol loses all its oxygen and two atoms of hydrogen in the form of water (H_2O_2), and a gaseous compound of carbon and hydrogen, (C_4H_4), which constitutes olefiant gas, is liberated. A similar hydrocarbon may be obtained from each of the other alcohols:

For example— $\overbrace{C_4H_6O_2}^{\text{Alcohol.}} - H_2O_2 = \overbrace{C_4H_4}^{\text{Oleft. Gas.}};$

and, generally, $C_nH_{n+2}O_2 - H_2O_2 = C_nH_n$.

General Formula =	C_nH_n	or	$C_nH_{n-1}H$
Methylene	C_2H_2	or	$C_2H.H$
Ethylene (Olefiant Gas)	C_4H_4	or	$C_4H_3.H$
Tritylene (Propylene)	C_6H_6	or	$C_6H_5.H$
Tetrylene (Oil Gas)	C_8H_8	or	$C_8H_7.H$
Amylene	$C_{10}H_{10}$	or	$C_{10}H_9.H$

7. *Aldehyds.*—If alcohol be distilled with oxide of manganese and diluted sulphuric acid, or with other oxidizing agents the oxidating influence of which can be applied with sufficient slowness and regularity, a very volatile liquid may be obtained (1077), each molecule of which contains the elements of one molecule of alcohol, minus 2 atoms of hydrogen. This substance is known as aldehyd. By similar means, corresponding compounds may be obtained from the other alcohols, these aldehyds possessing the

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* The necessity for doubling the formulæ of these bodies when isolated is explained in paragraph 1038.

General Formula,	$C_nH_nO_2$	or	$HO,C_nH_{n-1}O$
Formic aldehyd	$C_2H_2O_2$	or	HO,C_2HO
Acetic aldehyd	$C_4H_4O_2$	or	HO,C_4H_3O
Propionic aldehyd	$C_6H_6O_2$	or	HO,C_6H_5O
Butyric aldehyd (Butyral) .	$C_8H_8O_2$	or	HO,C_8H_7O
Valeric aldehyd (Valeral) .	$C_{10}H_{10}O_2$	or	$HO,C_{10}H_9O$

the action of oxygen in the proportion of O_2 upon 1 molecule of alcohol is to convert it into an aldehyd, with the removal of w in the proportion of H_2O_2;

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}}+O_2=\overbrace{C_4H_4O_2}^{\text{Aldehyd.}}+H_2O_2;$$

and, generally, $C_nH_{n+2}O_2+O_2=C_nH_nO_2+H_2O_2$.

8. *Homologous Volatile Acids.*—The aldehyds are neutral stances, but they rapidly absorb oxygen from the air, in the portion of O_2 for each molecule of the aldehyd, and thus bec converted into powerful hydrated acids, the general formul these hydrates being, $HO,C_nH_{n-1}O_3$, or $(C_nH_n)O_4$. These compounds are therefore derived by a process of oxidation f the alcohols; the formation of the aldehyd being the intermed stage in their production: each molecule of the alcohol, when a on by oxygen in the proportion of O_4, is converted into one m cule of the hydrate of a corresponding volatile acid, whilst 2 at of hydrogen are eliminated in the form of water.

$$\text{Thus,}\quad \overbrace{C_4H_6O_2}^{\text{Alcohol.}}+O_4=\overbrace{C_4H_4O_4}^{\text{Acetic Acid.}}+H_2O_2;$$

And, generally, $C_nH_{n+2}O_2+O_4=C_nH_nO_4+H_2O_2$.

The volatile fatty acids belong to this series, which is indeed m complete than that of the alcohols. A considerable number these acids exist in many of the vegetable and animal fats and o but chemists have not as yet succeeded in obtaining a gen method of reconverting the fatty acids into alcohols, though alcohols are readily converted into their corresponding acids. more important of these acids are the following:—

General Formula	= $HO,C_nH_{n-1}O_3$	or	$C_nH_nO_4$
Formic acid	HO,C_2HO_4	or	$C_2H_2O_4$
Acetic	$HO,C_4H_3O_3$	or	$C_4H_4O_4$
Propionic	$HO,C_6H_5O_3$	or	$C_6H_6O_4$
Butyric	$HO,C_8H_7O_3$	or	$C_8H_8O_4$
Valeric	$HO,C_{10}H_9O_3$	or	$C_{10}H_{10}O_4$
Caproic	$HO,C_{12}H_{11}O_3$	or	$C_{12}H_{12}O_4$
Œnanthylic	$HO,C_{14}H_{13}O_3$	or	$C_{14}H_{14}O_4$
Caprylic	$HO,C_{16}H_{15}O_3$	or	$C_{16}H_{16}O_4$
Pelargonic	$HO,C_{18}H_{17}O_3$	or	$C_{18}H_{18}O_4$
Capric	$HO,C_{20}H_{19}O_3$	or	$C_{20}H_{20}O_4$

Lauric	$HO,C_{24}H_{23}O_3$	or	$C_{24}H_{24}O_4$
Myristic	$HO,C_{28}H_{27}O_3$	or	$C_{28}H_{28}O_4$
Palmitic	$HO,C_{32}H_{31}O_3$	or	$C_{32}H_{32}O_4$
Stearic	$HO,C_{36}H_{35}O_3$	or	$C_{36}H_{36}O_4$
Cerotic	$HO,C_{54}H_{53}O_3$	or	$C_{54}H_{54}O_4$
Melissic	$HO,C_{60}H_{59}O_3$	or	$C_{60}H_{60}O_4$

Each molecule of acid corresponds to 4 volumes of vapour, (if O = 8 represent 1 vol.), and requires 1 equivalent of a base like potash for its saturation.

This group of acids, which is one of the most complete of the homologous series, illustrates in a very interesting manner the general similarity in properties which always exists in homologous bodies. This statement may appear paradoxical when the extreme terms of the series are compared together, since formic acid is an exceedingly pungent, corrosive, volatile liquid, which requires cooling below 32°, in order to render it solid, and it is miscible with water in all proportions; whilst melissic acid requires a temperature of 192° for its fusion, is insoluble in water, and has the properties of a fat: but if we compare together the contiguous terms of the series, such as the formic with the acetic, the acetic with the propionic acid, and so on, no abrupt change in properties will be perceived between the contiguous terms; each, as the proportion of carbon and hydrogen increases, becomes gradually less and less volatile, less fusible, less susceptible of solution in water, until we reach the true fatty acids. Now this similarity in properties, which is observed equally in other groups of homologous substances, naturally leads to the supposition that there must be a similarity in chemical constitution. It is not unreasonable to suppose that the acids $HO,C_nH_{n-1}O_3$, are all formed upon the plan or type of the simplest of them, viz., formic acid. Various theories may be advanced as to the composition of formic acid, but whatever that composition may be, we may imagine with Wurtz and with Gerhardt that the other acids are so many varieties of formic acid, which contain ethyl, trityl, tetryl, &c., instead of hydrogen; thus:—

Formic acid	$HO,C_2(H)O_3$
Acetic, or methylformic	$HO,C_2(C_2H_3)O_3$
Propionic, or ethylformic	$HO,C_2(C_4H_5)O_3$
Butyric, or tritylformic	$HO,C_2(C_6H_7)O_3$
Valeric, or tetrylformic	$HO,C_2(C_8H_9)O_3$

a somewhat similar hypothesis might be extended to the different alcohols themselves.

It will be perceived that all these groups, derived from the alcohols by decomposition, are produced by an analogous decomposition of the several alcohols, and that they all preserve a strict homology in their respective groups. This will be more easily traced by the aid of the Table below,* in which the different classes of compounds just described are so arranged that all those compounds which are placed in the same vertical column are homologous, whilst those which are placed in different columns are heterologous, or dissimilar in molecular constitution and in chemical characters: but it will be seen that those bodies in the same horizontal line are related to the same alcohol; they are all formed from it by reactions similar to those by which each of the corresponding compounds in the other horizontal lines are formed from their alcohol.

Exceptions to this uniformity occur in the last column, in the case of the compound ethers, the formula for which, in the majority of instances, represents the ether formed by the union of the acid with ethylic ether, since these compounds have been more generally formed and studied than any other kind of compound

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* *Table to illustrate the Arrangement of*

	Hydrocarbons. C_nH_n or $(C_nH_{n-1}H)$	Positive Radicles. C_nH_{n+1} or when free $(C_nH_{n+1})_2$	Simple Ethers. $C_nH_{n+1}O$ or when free $\left.\begin{matrix}C_nH_{n+1}\\C_nH_{n+1}\end{matrix}\right\}$	Sulphides. $C_nH_{n+1}S$ or when free $\left.\begin{matrix}C_nH_{n+1}\\C_nH_{n+1}\end{matrix}\right\}S_2$	Chlorides. $C_nH_{n+1}Cl$	Alcohols. $C_nH_{n+2}O_2$ or $\left.\begin{matrix}C_nH_{n+1}\\H\end{matrix}\right\}O_2$
1.	C_2H_2	$(C_2H_3)_2$	$(C_2H_3O)_2$	$(C_2H_3S)_2$	C_2H_3Cl	C_2H_3O,HO
2.	C_4H_4	$(C_4H_5)_2$	$(C_4H_5O)_2$	$(C_4H_5S)_2$	C_4H_5Cl	C_4H_5O,HO
3.	C_6H_6	$(C_6H_7)_2$			C_6H_7Cl	C_6H_7O,HO
4.	C_8H_8	$(C_8H_9)_2$	$(C_8H_9O)_2$		C_8H_9Cl	C_8H_9O,HO
5.	$C_{10}H_{10}$	$(C_{10}H_{11})_2$	$(C_{10}H_{11}O)_2$	$(C_{10}H_{11}S)_2$	$C_{10}H_{11}Cl$	$C_{10}H_{11}O,HO$
6.	$C_{12}H_{12}$	$(C_{12}H_{13})_2$				$C_{12}H_{13}O,HO$
7.						
8.	$C_{16}H_{16}$				$C_{16}H_{17}Cl$	$C_{16}H_{17}O,HO$
9.	$C_{18}H_{18}$					
10.	$C_{20}H_{20}$					
11.						
12.						$C_{24}H_{25}O,HO$
13.						
14.						
15.						
16.	$C_{32}H_{32}$		$(C_{32}H_{33}O)_2$	$(C_{32}H_{33}S)_2$	$C_{32}H_{33}Cl$	$C_{32}H_{33}O,HO$
17.						
18.						
19.						
20.						
27.	$C_{54}H_{54}$					$C_{54}H_{55}O,HO$
30.	$C_{60}H_{60}$					$C_{60}H_{61}O,HO$
Relation to Hydrogen		H or $\left.\begin{matrix}H\\H\end{matrix}\right\}$	HO or $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$	HS or $\left.\begin{matrix}H\\H\end{matrix}\right\}S_2$	HCl	2 HO or $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$

ether; though in a few instances the compound ether resulting from the union of the acid of the series with its corresponding ether, is given, and there can be no doubt that such ethers might in all cases be formed if any sufficient inducement to their preparation existed; or if the materials required were sufficiently abundant.

The column headed *Mercaptans* contains a series of compounds which correspond to the alcohols, and are strictly analogous to them; they contain sulphur in the place of oxygen: the *sulphides* are analogous in like manner to the ethers; and the *bromides* and *iodides*, which however are not included in the table, are analogous to the chlorides. The quantities represented by the formulæ given in the table yield, in all cases where the compound is volatile without decomposition, 4 volumes of vapour if O = 8 be taken as 1 vol. In this table many blanks occur, which could in most cases be filled up if the compounds which correspond

mpounds in Homologous Series.

Mercaptans.	Aldehyds.	Volatile Acids.	Compound Ethers.	
$C_nH_{n+2}S_2$ or $\left.\begin{matrix}C_nH_{n+1}\\H\end{matrix}\right\}S_2$	$C_nH_nO_2$ or $\left.\begin{matrix}C_nH_{n-1}O_2\\H\end{matrix}\right\}$	$C_nH_nO_4$ or $HO,C_nH_{n-1}O_3$	$C_nH_{n+1}O,C_nH_{n-1}O_3$ or $\left.\begin{matrix}C_nH_{n+1}\\C_nH_{n-1}O_2\end{matrix}\right\}O_2$	
C_2H_3S,HS	$C_2H\ O,HO$	$HO,C_2H\ O_3$	$C_2H_3O,C_2H\ O_3$	1.
C_4H_5S,HS	C_4H_3O,HO	$HO,C_4H_3O_3$	$C_4H_5O,C_4H_3O_3$	2.
	C_6H_5O,HO	$HO,C_6H_5O_3$	$C_4H_5O,C_6H_5O_3$	3.
C_8H_9S,HS	C_8H_7O,HO	$HO,C_8H_7O_3$	$C_4H_5O,C_8H_7O_3$	4.
$C_{10}H_{11}S,HS$	$C_{10}H_9O,HO$	$HO,C_{10}H_9O_3$	$C_{10}H_{11}O,C_{10}H_9O_3$	5.
	$C_{12}H_{11}O,HO$	$HO,C_{12}H_{11}O_3$	$C_4H_5O,C_{12}H_{11}O_3$	6.
	$C_{14}H_{13}O,HO$	$HO,C_{14}H_{13}O_3$	$C_4H_5O,C_{14}H_{13}O_3$	7.
		$HO,C_{16}H_{15}O_3$	$C_4H_5O,C_{16}H_{15}O_3$	8.
		$HO,C_{18}H_{17}O_3$	$C_4H_5O,C_{18}H_{17}O_3$	9.
	$C_{20}H_{19}O,HO$	$HO,C_{20}H_{19}O_3$	$C_4H_5O,C_{20}H_{19}O_3$	10.
				11.
		$HO,C_{24}H_{23}O_3$	$C_4H_5O,C_{24}H_{23}O_3$	12.
				13.
		$HO,C_{28}H_{27}O_3$	$C_4H_5O,C_{28}H_{27}O_3$	14.
				15.
$C_{32}H_{33}S,HS$	$C_{32}H_{31}O,HO$	$HO,C_{32}H_{31}O_3$	$C_{32}H_{33}O,C_{32}H_{31}O_3$	16.
				17.
		$HO,C_{36}H_{35}O_3$	$C_4H_5O,C_{36}H_{35}O_3$	18.
				19.
		$HO,C_{40}H_{39}O_3$		20.
		$HO,C_{54}H_{53}O_3$	$C_{54}H_{55}O,C_{54}H_{53}O_3$	27.
		$HO,C_{60}H_{59}O_3$		30.
2 HS or $\left.\begin{matrix}H\\H\end{matrix}\right\}S_2$	$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$	$\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$	

to them presented sufficient interest to induce the chemist to prepare them. New compounds are indeed being continually added to the list. By thus mapping out the territory which has been explored, the progress of future research is materially aided, and each new compound, as it is discovered, more readily falls into its true place, while its relations to other bodies previously known are anticipated, and readily verified.

Exact observations upon the crystalline form of homologous bodies are still wanted; but it appears that in many cases homologous compounds are isomorphous, though this is not by any means uniformly true. The methyl-sulphate and ethyl-sulphate of baryta appear to be isomorphous; such is the case also with the alums formed with sulphate of alumina by the sulphates of the alcohol bases, methylia, ethylia, amylia, and trimethylia; but the double salts formed by the chlorides of these bases with bichloride of platinum are decidedly not isomorphous. The double salt of hydrochlorate of trimethylia and bichloride of platinum is isomorphous with the corresponding salt of ammonia; but the corresponding double salt of ethylia crystallizes in rhombohedra, and that of diethylia in oblique prisms.

(917) *Theory of Compound Radicles.*—Liebig explained the similarity in properties between the terms of homologous series by supposing the existence in each, of a certain group of elements which he regarded as the radicle of the series. He, in fact, made the theory of *compound radicles*,* as it is termed, the basis of his classification, and defined organic chemistry to be the chemistry of compound radicles. According to this supposition, the basis of each ether is a hydrocarbon, from which all the *heterologous* bodies of the series, or bodies not analogous in composition, are derived: for example,

Compound Radicle.		*Ether, or Oxide of the Radicle.*	
Methyl	$(C_2\,H_3)$	Methylic Ether .	$(C_2\,H_3)O$
Ethyl	$(C_4\,H_5)$	Ethylic Ether .	$(C_4\,H_5)O$
Amyl	$(C_{10}H_{11})$	Amylic Ether .	$(C_{10}H_{11})O$

Alcohol, or Hydrated Oxide.		*Compound Ether.*	
Wood Spirit	$(C_2\,H_3)\,O,HO$	Formiate of Methyl .	$(C_2\,H_3)\,O,(C_2\,H)\,O_3$
Alcohol . .	$(C_4\,H_5)\,O,HO$	Acetate of Ethyl . .	$(C_4\,H_5)\,O,(C_4\,H_3)O_3$
Fousel Oil .	$(C_{10}H_{11})O,HO$	Valerate of Amyl. .	$(C_{10}H_{11})O,(C_{10}H_9)O_3$

Upon this theory the simple ethers are oxides of the peculiar electro-positive hydrocarbon (p. 48) which forms the radicle of the series;

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* The German term *radikal* is commonly, but inaccurately translated *radical*, which is properly an adjective, the word *radicle* being the appropriate rendering. To some, this objection may appear to be hypercritical; but accuracy in the use of terms can scarcely be observed too closely.

the alcohols are the hydrated oxides of the same radicle, and the so-called hydrochloric, hydrobromic, hydriodic, and hydrosulphuric ethers, are compounds in which chlorine, bromine, iodine, or sulphur have taken the place of the oxygen of the ordinary ether, —just as in the compounds of a metal, the chlorine, the iodine, or the sulphur, displaces the oxygen; whilst the compound group termed ethyl (C_4H_5) discharges a function in these compounds analogous to that of potassium in its salts: thus, calling ethyl (C_4H_5) = Et., the two series would run as follows:—

Oxide of potassium	KO	Oxide of ethyl .	EtO
Chloride of potassium	KCl	Chloride of ethyl .	EtCl
Iodide of potassium	KI	Iodide of ethyl .	EtI
Sulphide of potassium	KS	Sulphide of ethyl .	EtS

The mercaptans correspond in composition to alcohol in which the place of the oxygen is supplied by sulphur; whilst the compound ethers, such as the formic, the acetic, and the valeric, are regarded in the light of salts, in which the formic, the acetic, or valeric acid is combined with the oxide of methyl, of ethyl, or of some other compound radicle, by which its acid properties are completely neutralized.

The aldehyds and acids are regarded as belonging to a different series, which contains a different organic radicle possessed of electro-negative properties: for instance,

Compound Radicle.	Hydrated Oxide, or Aldehyd.	Intermediate Acid.	Hydrated Volatile Acid.	Perchloride.
Formylic (C_2H)	Formic Aldehyd $\}$ $(C_2H)O,HO$		Formic $HO,(C_2H)O_3$	Chloroform $\}$ $(C_2H)Cl_3$
Acetylic (C_4H_3)	Acetic Aldehyd $\}$ $(C_4H_3)O,HO$	Aldehylic Acid $HO,(C_4H_3)O_3$	Acetic $HO,(C_4H_3)O_3$	
Valerylic ($C_{10}H_9$)	Valeric Aldehyd $\}$ $(C_{10}H_9)O,HO$		Valeric $HO,(C_{10}H_9)O_3$	

The formula for the radicle of each of these electro-negative series, it will be seen, differs from that of the radicle of the alcohol from which they are produced by 2 atoms of hydrogen: methyl (C_2H_3) by the loss of 2 atoms of hydrogen yielding the elements of the formylic radicle (C_2H); ethyl minus 2 atoms of hydrogen, furnishing the elements of the acetylic radicle, and so on.

It is true that the theory of compound radicles supposes the existence of a number of substances which have not been isolated, and also of many which probably have no separate existence. The theory indeed cannot be supposed to afford a correct representation of the molecular constitution of organic bodies; but it is a convenient fiction, which materially facilitates the retention of their composition in the memory, and the comprehension of the metamorphoses which such compounds experience. One of the first groups to which it was systematically applied by Liebig and Wöhler was that derived from the essential oil of bitter almonds. This oil was regarded by these chemists as containing an organic radicle, to which they gave the name of benzoyl ($C_{14}H_5O_2$), and which may be conveniently distinguished by the symbol Bz. Although unsuccessful in the attempt to isolate this radicle, they succeeded in transferring the group of which it was supposed to consist, from one elementary substance to another, and in causing it to enter into combination with other organic groups; and by the aid of this hypothesis they were enabled to give as simple and intelligible an account of the mode in which the compounds derived from it were formed, as though they had been dealing with the salts or other compounds of a metal. The advantages thus obtained may be rendered evident by comparing the empirical formulæ of these compounds with those in which the organic radicle is assumed to be present:—

	Empirical Formula.	$C_{14}H_5O_2$=Bz	
Oil of Bitter Almonds .	$C_{14}H_6O_2$	BzH,	Hydride of Benzoyl
Benzoic Acid	$C_{14}H_6O_4$	HO,BzO,	Oxide of Benzoyl
Chlorinated Compound .	$C_{14}H_5O_2Cl$	BzCl,	Chloride of Benzoyl
Sulphur Compound . .	$C_{14}H_5O_2S$	BzS,	Sulphide of Benzoyl
Cyanogen Compound .	$C_{16}H_5O_2N$	BzCy,	Cyanide of Benzoyl

It is, moreover, to be observed, that many substances corresponding in composition to certain of the organic radicles may be isolated. The existence of cyanogen as an electro-negative organic radicle, and the remarkable analogy in its mode of combination to that of chlorine and the halogens, were known long before Liebig had attempted to generalize the theory of organic radicles. Bunsen subsequently isolated kakodyl (C_4H_6As), which is an excellent representative of the electro-positive class of radicles, and other bodies of analogous composition have since been obtained; whilst several compounds having the composition of such radicles as ethyl and methyl, which are supposed to form the bases of the alcohols and ethers, have been obtained in a separate form by the valuable researches of Frankland and others.

(918) *Theory of Isolated Radicles—Atoms and Molecules.*—The recent progress of research has rendered it very probable that the bodies thus isolated are not really the radicles that they were once supposed to be. Later writers indeed usually follow Gerhardt who expressly rejects isolability as constituting any part of his idea of a radicle (*Traité*, t. iv. p. 569). He says: "Let it be clearly understood that, in speaking of a radicle, I do not indicate

any substance under the form and with the properties which it would have in an isolated condition; but I distinguish by it simply the proportion in which certain elements, or groups of elements, may be substituted for others, or may be transferred from one body to another in the process of double decomposition."

Bodies when in combination present characters and properties very different from those which they exhibit in what is usually regarded as their free or isolated condition. The affinities of bodies in their 'nascent state,' or at the moment of their liberation from combination with others, are by all chemists admitted to be much more active than those which they possess in their 'free state.'

In fact, it appears to be highly probable, as supposed by Brodie (863, *note*) and strongly urged by Gerhardt and his followers, that few, if any, elementary substances in their uncombined condition are in reality known to us,—the so-called elementary bodies being really compounds of at least two atoms of the true element with each other. Hydrogen gas, for example, is not simply H, but is H_2 or $\left.\begin{matrix}H\\H\end{matrix}\right\}$, or hydride of hydrogen; metallic potassium is not simply K, but K_2, or $\left.\begin{matrix}K\\K\end{matrix}\right\}$, or potasside of potassium; in like manner chlorine gas is $\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}$, or chloride of chlorine. This view has also been extended to the so-called compound organic radicles; cyanogen gas being not C_2N, but $\left.\begin{matrix}C_2N\\C_2N\end{matrix}\right\}$, or cyanide of cyanogen; and liquid kakodyl is $\left.\begin{matrix}Kd\\Kd\end{matrix}\right\}$, or kakodylide of kakodyl. Indeed, it admits of experimental proof in many cases, as in that of methyl (1038), that the compound must be thus doubled, methyl being truly $\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}$, or methylide of methyl; ethyl being $\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}$, or ethylide of ethyl; acetic anhydride, $\left.\begin{matrix}C_4H_3O_3\\C_4H_3O_3\end{matrix}\right\}$, or acetic acetate; and so on.

The important influence which this view has exerted and is still exerting upon the progress of the science, renders it necessary to develope it somewhat further.

In order to give precision to our language, it will be convenient here to draw a distinction between two magnitudes of the component particles of all elementary bodies, viz. 1. The *Atom*,—or smallest and chemically indivisible particle of each element which can exist in a *compound* united with other particles either of the same or of different

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to be present :—

Oil of Bitter Almonds
Benzoic Acid
Chlorinated Compound
Sulphur Compound
Cyanogen Compound

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should be thus represented :—

$$= \left.\begin{matrix}H\\Cl\end{matrix}\right\} + \left.\begin{matrix}H\\Cl\end{matrix}\right\};$$

one of the atoms of hydrogen in the
places with one of the atoms of
chlorine gas: and the result is, the
of hydrochloric acid gas.
view, it has been stated as a uniform
all the reactions in which chlorine
is known in which less than two atoms
for example, the successive steps of
Dutch liquid (400) :—

$$=C_4H_3Cl_3+HCl$$
$$=C_4H_2Cl_4+HCl$$
$$=C_4H\,Cl_5+HCl$$
$$=C_4\quad Cl_6+HCl$$

And the same is true in all other cases. Hence it has been concluded that the smallest particle of chlorine which can exist in the free state—its molecule, in short—must contain two atoms of chlorine.

A similar necessity for the presence of at least two atoms of bromine, and of iodine, has been observed in every reaction in which they take part; and the same thing is true of hydrogen and of all the metals which correspond to hydrogen in atomic character. When, for instance, a molecule of one of these metals is made to act upon any compound body, double decomposition occurs; thus if the case be taken in which chloride of kakodyl is decomposed by means of zinc, the decomposition should be represented as occurring in two stages, as follows:—

$$\left.\begin{matrix}\mathrm{Kd}\\\mathrm{Cl}\end{matrix}\right\}+\left.\begin{matrix}\mathrm{Zn}\\\mathrm{Zn}\end{matrix}\right\}=\left.\begin{matrix}\mathrm{Zn}\\\mathrm{Cl}\end{matrix}\right\}+\left.\begin{matrix}\mathrm{Zn}\\\mathrm{Kd}\end{matrix}\right\};\ \text{and}\ \left.\begin{matrix}\mathrm{Zn}\\\mathrm{Kd}\end{matrix}\right\}+\left.\begin{matrix}\mathrm{Kd}\\\mathrm{Cl}\end{matrix}\right\}=\left.\begin{matrix}\mathrm{Zn}\\\mathrm{Cl}\end{matrix}\right\}+\left.\begin{matrix}\mathrm{Kd}\\\mathrm{Kd}\end{matrix}\right\}.$$

In such reactions the existence of the intermediate compound corresponding to $\left.\begin{matrix}\mathrm{Zn}\\\mathrm{Kd}\end{matrix}\right\}$ cannot, however, always be traced, as such combinations are usually of small stability and are decomposed as rapidly as they are formed.

When, for instance, hydrochloric acid is decomposed by means of zinc, the intermediate hydride of zinc has not been observed; though analogy would lead us to represent the change by the following equations:—

$$\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}+\left.\begin{matrix}\mathrm{Zn}\\\mathrm{Zn}\end{matrix}\right\}=\left.\begin{matrix}\mathrm{Zn}\\\mathrm{Cl}\end{matrix}\right\}+\left.\begin{matrix}\mathrm{Zn}\\\mathrm{H}\end{matrix}\right\};\ \text{and}\ \left.\begin{matrix}\mathrm{Zn}\\\mathrm{H}\end{matrix}\right\}+\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}=\begin{matrix}\mathrm{Zn}\\\mathrm{Cl}\end{matrix}+\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}.$$

It is indeed upon the formation of such intermediate compounds, that the most probable inference respecting the magnitude of the molecule of a body is founded; for in no case can any such intermediate compound be formed, unless two atoms of each of the original bodies concerned in the reaction take part in the metamorphoses under consideration. For example, it is hence urged that the molecule of ethylic (or ordinary) ether cannot be less than (C_4H_5O,C_4H_5O) because of the existence of the compound methyl-ethyl ether, which is a body intermediate between ethylic ether and methylic ether: for we have

$$1.\ \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}}^{\text{Ethylic ether.}}\quad;\quad 2.\ \overbrace{\left.\begin{matrix}C_2H_3\\C_4H_5\end{matrix}\right\}}^{\text{Methyl-ethylic ether.}}\quad;\quad 3.\ \overbrace{\left.\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right\}}^{\text{Methylic ether.}}$$

In like manner many chemists regard the hydrates as compounds intermediate between water and the anhydrous oxides:—

1. HHO_2 water	HHO_2 water.
2. KHO_2 hydrate of potash	$HZnO_2$ hydrated oxide of zinc
3. KKO_2 anhydrous potash	$ZnZnO_2$ anhydrous oxide of zinc

And upon this view an argument has been founded for regarding the formula of water as H_2O_2, and not as HO.

It must not, however, be supposed that there is no such thing as direct combination between two bodies: the molecules of compounds frequently exhibit the power of uniting in this manner, whilst the number of molecules of the new body is smaller than the sum of those of its components: in other words, condensation occurs. Thus, when 1 molecule of carbonic oxide and 1 of chlorine unite, they form 1 molecule of oxychloride of carbon; $C_2O_2+Cl_2$, yielding $C_2O_2Cl_2$. In like manner, ammonia and hydrochloric acid gases combine directly; H_3N+HCl becoming H_4NCl. Deutoxide of nitrogen with oxygen forms peroxide of nitrogen; NO_2+O_2 becoming NO_4. Terchloride of antimony and chlorine yield the pentachloride of antimony; $SbCl_3+Cl_2=SbCl_5$. It may indeed be stated as a general rule, that whenever a body formed upon the type of ammonia combines with a body formed on the type of hydrochloric acid, that direct or additive combination occurs: though these are not the only compounds which exhibit this tendency; for example, aldehyd ($C_4H_4O_2$) combines directly with O_2 to form acetic acid, ($C_4H_4O_4$). Double salts belong to a different category, although nearly always formed by this additive process, as when bichloride of platinum and chloride of potassium unite, $KCl+PtCl_2$ yielding $KCl,PtCl_2$: because, so far as we know, such combination exists only so long as the compound is in the solid form; whereas the other bodies, previously cited, are known in the aëriform condition, in which state the relations by volume of the molecules of different compounds are definite, whilst we know but little of the relative volumes of solid molecules.

(919) *Arguments for doubling the Atomic Weight of Oxygen.*—The distinction which has just been pointed out between th atom and the molecule of a body is intimately connected with th alterations proposed by Gerhardt in the values to be assigned t the atomic weights of some of the elements. It will therefore b convenient to advert here to the principal arguments which hav been advanced upon this point.

As already stated (896) Gerhardt doubles the atomic weight o oxygen, of sulphur, and of carbon, as well as of one or two othe less important elements.

In support of this measure it is urged in the case of oxyge and sulphur, for example, that there is a marked distinction between the number of the compounds which these elements form with other bodies, when such compounds are compared with the compounds which chlorine and bromine are known to form with the same bodies:—so that there are numerous oxides and sulphides which have no corresponding representatives among the chlorides and bromides. This fact will be rendered evident by an examination of the following table, where a certain number of the compounds of each of these elements are enumerated:—

	Oxides.	Sulphides.	Chlorides.	Bromides.
1.	Water HHO_2	Sulphuretted hydrogen HHS_2	Hydrochloric acid HCl	Hydrobromic acid HBr
2.	Hydrate of potash KHO_2	Sulphhydrate potass. HKS_2	Wanting.	
3.	Anhydrous potash KKO_2	Sulphide of potassium KKS_2	Chloride of potassium KCl	Bromide of potassium KBr
4.	Alcohol $(C_4H_5)H,O_2$	Mercaptan $(C_4H_5)H,S_2$	Wanting.	
5.	Potassium alcohol $(C_4H_5)K,O_2$	Mercaptide potassium $(C_4H_5)K,S_2$	Wanting.	
6.	Ether $(C_4H_5)(C_4H_5)O_2$	Sulphide of ethyl $(C_4H_5)(C_4H_5)S_2$	Chloride of ethyl $(C_4H_5)Cl$	Bromide of ethyl $(C_4H_5)Br$
7.	Acetic acid $(C_4H_3O_2)H,O_2$	Thiacetic acid $(C_4H_3O_2)H,S_2$	Wanting.	
8.	Acetate of lead $(C_4H_3O_2)Pb,O_2$	Thiacetate of lead $(C_4H_3O_2)Pb,S_2$	Wanting.	
9.	Acetic ether $(C_4H_3O_2)(C_4H_5)O_2$	Thiacetic ether $(C_4H_3O_2)(C_4H_5)O_2$	Wanting.	
10.	Acetic anhydride $(C_4H_3O_2)(C_4H_3O_2)O_2$	Thiacetic anhydride $(C_4H_3O_2)(C_4H_3O_2)S_2$	Acetic oxychloride $(C_4H_3O_2)Cl$	Acetic oxybromide $(C_4H_3O_2)Br$

In all cases, intermediate oxides and sulphides, such as those shown at 2, 4, 5, 7, 8, and 9, may be traced, whilst in no case can any intermediate chlorides or bromides be formed: in other words, two different radicles may be united into one compound when oxygen or sulphur is combined with them; whilst this is never the case with chlorine or with bromine. Hence it is argued, that the quantities of oxygen and of sulphur indicated by O_2 and S_2 in the foregoing formulæ are not really two atoms, but rather that they represent an indivisible whole, or, in fact, *one* atom. In consequence of this, two atoms of each of the other elements or radicles are united with O_2 or S_2, and are held together as one group, owing to the indivisibility of the quantities of the elements represented by the symbols O_2 and S_2. On the other hand, the non-existence of such intermediate compounds, or compounds containing two *different* elements or radicles, amongst the chlorides and the bromides is an indication that no such cause of union exists in the atomic constitution of chlorine and of bromine, but that the quantities represented respectively by the symbols Cl and Br correspond truly to the atoms of these bodies.

The different metamorphoses which many bodies undergo under the influence, on the one hand, of certain sulphuretted, and on the other of certain chlorinated compounds, have been further adduced in support of this view.

When, for instance, alcohol or acetic acid is acted upon by a sulphuretted body such as pentasulphide of phosphorus, a *single* new sulphuretted body is formed; but when the same compounds are acted upon by a body which furnishes chlorine, such as pentachloride of phosphorus, *two* new chlorinated derivatives are produced, thus:—

$$\overbrace{(C_4H_5)H,O_2}^{\text{Alcohol.}} + PS_5 = \overbrace{(C_4H_5)H,S_2}^{\text{Mercaptan.}} + \overbrace{PS_3O_2}^{\text{Oxysulphide phosphorus.}};$$

$$\overbrace{(C_4H_3O_2)H,O_2}^{\text{Acetic acid.}} + PS_5 = \overbrace{(C_4H_3O_2)H,S_2}^{\text{Thiacetic acid.}} + PS_3O_2;$$

whilst

$$\overbrace{(C_4H_5)\ H,O_2}^{\text{Alcohol.}} + PCl_5 = [\overbrace{(C_4H_5)\ Cl_2}^{\text{Chloride of ethyl.}} \text{ and } \overbrace{HCl}^{\text{Hydrochloric acid.}}] + \overbrace{PCl_3O_2}^{\text{Oxychloride phosphorus.}}$$

$$\overbrace{(C_4H_3O_2)H,O_2}^{\text{Acetic acid.}} + PCl_5 = [\overbrace{(C_4H_3O_2)\ Cl}^{\text{Acetic oxychloride.}} \text{ and } HCl] + PCl_3O_2.$$

The groups C_4H_5 and H, on the one hand, and the groups C_4H_3 and H, on the other, are held together by the indivisible quant O_2 or S_2; whilst they separate into two distinct bodies as soon chlorine takes the place of the oxygen, because the quantity chlorine (Cl_2) which displaces the quantity of oxygen (O_2) is rea not a single atom, but two atoms.

Analogous reasoning may be extended to the case of compounds of carbon, the ordinary atomic weight of which it proposed also to double on similar grounds.

Selenium and tellurium, from their analogy with sulphur, i supposed should also be indicated with doubled atomic weigh and some chemists would also double that of silicon and of cert of the metals; but the arguments are less definitely applicable in these instances.

In order to distinguish these new atomic weights from those in common use, they may be indicated by the employment of barred letters in the following manner:—

Oxygen $\Theta=16$	Selenium $\text{Ꞩe}=79{\cdot}5$
Sulphur $\text{Ꞩ}=32$	Carbon $\text{Ȼ}=12$

It may be remarked, that if it be desired to translate formulæ written with the new symbols into those ordinarily employed, it is simply necessary to multiply the numbers of the atoms of oxygen, sulphur, and carbon by 2; for instance:—

$$\overbrace{\text{Ȼ}_2H_4\Theta_2}^{\text{Acetic acid.}}=C_4H_4O_4\text{; and }\overbrace{KH\text{Ꞩ}\Theta_4}^{\text{Bisulph. potash.}}=KHS_2O_8.$$

(920) *On the Use of Molecular Formulæ.*—It is obvious that if $\Theta=16$, the smallest particle of water which can exist must be represented by the formula $H_2\Theta=H_2O_2$: and in like manner the formula for sulphuretted hydrogen expressing its atom must be $H_2\text{Ꞩ}=H_2S_2$; consequently, the formulæ $H_2\Theta$ and $H_2\text{Ꞩ}$ constitute the atomic as well as the molecular formulæ of these bodies.

The *atomic weights* of the elements are, however, to be carefully distinguished from their *molecular weights*, the atomic weights being the numbers which represent the relative weights of the atoms of the different elements, when referred to some arbitrary but recognised standard; whilst the molecular weights, whether of the elements or of compounds, represent the relative weights of the molecules; and the molecular weight, when once the magnitude of the molecule is agreed upon, is determined by the sum of the weights of all the atoms which enter into the formation of the molecule itself. The molecular formula of a compound body may frequently be ascertained by considerations analogous to those adduced in the cases of water and of sulphuretted hydrogen. In other instances material aid is obtained by an examination of the density of its vapour, for it has been ascertained to be a rule to which very few exceptions are known,* that when the vapours of compound bodies are compared under similar circumstances of temperature and pressure, equal volumes of the different compounds contain an equal number of their constituent molecules, or, in other words, that the molecules of all compounds furnish equal volumes of vapour; consequently, the densities of the vapours are exactly in the ratio of their molecular weights.

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* Among these exceptions are chlorous acid and some of the oxides of nitrogen.

Allusion has already been made (913) to the facility which a knowledge of this law gives to the calculation of the vapour density of a body from its molecular formula; and, conversely, to the valuable control which the vapour density affords to the calculated molecular formula. The simplicity thus introduced into our calculations of vapour volume affords a strong argument in favour of the uniform employment of molecular formulæ in our ordinary equations for the representation of chemical changes: by such a method the gaseous volume of each constituent is thus at once placed before the eye. If we continue to assume as the unit of volume that of oxygen, O, with the atomic weight of 8, the volume of hydrogen, H, will represent twice that bulk, whilst the molecule of hydrogen, or H_2, will represent 4 volumes. Now the gaseous volume occupied by each molecule of any compound will (with the exceptions already specified) also occupy 4 volumes.*

For example, the formulæ H_2 and Cl_2 each represent a molecule of hydrogen and chlorine respectively, whilst HCl represents a molecule of hydrochloric acid; and we see by the equation $H_2+Cl_2=2HCl$, that a molecule of hydrogen and one of chlorine unite without condensation to form 2 molecules of hydrochloric acid; whilst, when oxygen and hydrogen unite to form water, from the equation

$$O_4+2\,H_2=2\,H_2O_2;\ \text{or,}$$
$$\Theta_2+2\,H_2=2\,H_2\Theta,$$

it is manifest that 1 molecule of oxygen and 2 molecules of hydrogen unite to form 2 molecules of steam, and that the 3 volumes which the gases occupied in their separate condition become condensed into 2 when they have united.

So, again, it is clear from the equation employed, that a similar condensation occurs when carbonic oxide and oxygen unite to form carbonic acid; for

$$O_4+2\,C_2O_2=2\,C_2O_4;\ \text{or,}$$
$$\Theta_2+2\,\text{€}\Theta=2\,\text{€}\Theta_2;$$

1 molecule of oxygen and 2 of carbonic oxide yielding 2 molecules of carbonic acid.

Again, when marsh gas is detonated with oxygen, the formula at once gives the volume of oxygen required, and the gaseous products which are obtained :—

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* Gerhardt takes hydrogen (H) as the unit of volume; consequently (H_2), or the molecule of free hydrogen, with him represents 2 volumes, and all compounds in like manner have a molecular volume of 2, which simplifies the matter considerably.

$$2\,O_4 + C_2H_4 = C_2O_4 + 2\,H_2O_2\text{; or}$$
$$2\,\Theta_2 + \text{Ȼ}H_4 = \text{Ȼ}\Theta_2 + 2\,H_2\Theta.$$

2 volumes of oxygen and 1 volume of marsh gas yielding 1 of carbonic acid and 2 of steam; whilst if olefiant gas be detonated with oxygen, we find

$$3\,O_4 + C_4H_4 = 2\,C_2O_4 + 2\,H_2O_2\text{; or}$$
$$3\,\Theta_2 + \text{Ȼ}_2H_4 = 2\,\text{Ȼ}\Theta_2 + 2\,H_2\Theta:$$

showing that 3 volumes of oxygen and 1 volume of olefiant gas furnish 2 volumes of carbonic acid and 2 of steam.

It is obvious that this facility of expression and simplicity in the interpretation of results afford a powerful recommendation of the employment of formulæ which represent uniform volumes of vapour in the description of chemical metamorphoses. We shall hereafter, wherever it is practicable, avail ourselves of these advantages, and shall adopt the use of 4-volume molecular formulæ, retaining the customary atomic weights for oxygen, sulphur, and carbon, except on particular occasions, where the employment of the new symbols may be requisite for the more complete elucidation of the views of Gerhardt and his followers.*

(921) *Chemical Types.*—The homologous series of the alcohols which has already been briefly reviewed (916) has its representatives among the simpler compounds contained in the department of inorganic chemistry; for by deducting 2 (C_2H_2) from methyl and the compounds of the methylic group (contained in the horizontal line 1 in the Table), we arrive at hydrogen and some of its most important compounds of simple constitution. Thus the molecule of methyl, if deprived of 2 C_2H_2, would leave a residue consisting only of hydrogen; $(C_2H_3)_2 - 2\ C_2H_2 = H_2$. The molecule of methylic ether deprived of 2 C_2H_2 would leave water; $(C_2H_3O)_2 - 2\ C_2H_2 = H_2O_2$: the residue from each molecule of the sulphide of methyl and of methylic mercaptan would be sulphuretted hydrogen. Chloride of methyl after a deduction of C_2H_2 would become hydrochloric acid. Hence it appears that the radicles methyl, ethyl, trityl, tetryl, amyl, &c., are bodies which correspond to hydrogen, and that they may be regarded as

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* It has been already intimated that the formulæ which express the composition of salts cannot in strictness be regarded as molecular formulæ, or formulæ of uniform vapour volumes. They indicate *solid* not *gaseous* molecules, and only represent the proportional quantity of each constituent.

[illegible] hydrogen forms the lowest term; [illegible] are homologues of water, whilst [illegible] are homologues of hydrochloric and [illegible] and mercaptans are homologues [illegible] water, hydrochloric, and hydrosulphuric [illegible] or *types* upon which these several [illegible]

[illegible] organic compounds to some simple [illegible] been systematically worked out by [illegible]

[illegible] types to which the latter chemist refers [illegible] organic chemistry are the following:—

[illegible] hydrogen type . $\left.\begin{matrix}H\\H\end{matrix}\right\}$ or H_2

[illegible] hydrochloric acid type $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$

[illegible] water type . . . . . $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$

[illegible] ammonia type . . . $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$

[illegible] remark, that many bodies are referred to the [illegible] present no analogy in chemical properties, [illegible] each other. The various radicles which have [illegible] assumed to exist in organic compounds vary in [illegible] the elementary bodies themselves. Some, [illegible] being strongly electro-negative, may be [illegible] oxygen, and sulphur, on the right hand [illegible] arranging series; such as the following:—

POTASSIUM. CHLORINE.
SODIUM. OXYGEN.
CALCIUM. SULPHUR.
IRON. GOLD.
&c. &c.
ANTIMONY.
ARSENIC:

[illegible] aldehyd and acetone, agree with arsenic and [illegible] occupying a central or intermediate position; and [illegible] kakodyl (C_4H_6As) and the metallic derivatives [illegible] arranged with the electro-positive bodies, [illegible] calcium, &c., on the left hand side of such [illegible] a series. When we compare together different compounds belonging to the same series, a progressive change in properties is observed, so that the differences observable between any two such compounds become greater, the wider is the interval between the respective places in the series of the two terms submitted to the comparison. Following this idea to its extreme limits, the same type may therefore comprehend bodies belonging to the three classes of acids, of bases, and of neutral bodies; the acids or electro-negative bodies being at one extremity of the series, and the neutral bodies occupying the intermediate positions, provided that the bases or electro-positive bodies be arranged at the opposite extremity.

These types are to be regarded as *types of double decomposition;* and are chiefly useful as representing the fact that the bodies which are referred to them experience a similar mode of decomposition when subjected to the action of the same chemical reagents.

The application of these types to the compounds of organic chemistry will be best understood by means of a few examples:—

1. The hydrogen or metallic type $\left\{\begin{matrix}H\\H\end{matrix}\right.$

To this class Gerhardt refers amongst the compounds of inorganic chemistry, the metals, together with the hydrides, arsenides, and antimonides of the metals; and amongst organic compounds, the radicles of the alcohols, the hypothetical oxidized radicles of certain acids, marsh gas, and the hydrocarbons homologous with it, the aldehyds, &c.—*e. g.*:

	Methyl (methylide of methyl) . . .	$\left\{\begin{matrix}C_2H_3\\C_2H_3\end{matrix}\right.$
	Ethyl (ethylide of ethyl)	$\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
	Marsh gas (hydride of methyl) . .	$\left\{\begin{matrix}C_2H_3\\H\end{matrix}\right.$
	Hydride of amyl	$\left\{\begin{matrix}C_{10}H_{11}\\H\end{matrix}\right.$
Hypothetical.	Acetyl	$\left\{\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right.$
	Benzoyl	$\left\{\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right.$
	Aldehyd (hydride of acetyl) . . .	$\left\{\begin{matrix}C_4H_3O_2\\H\end{matrix}\right.$
	Acetone (methylide of acetyl) . . .	$\left\{\begin{matrix}C_4H_3O_2\\C_2H_3\end{matrix}\right.$

The hydrochloric acid type $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$ is now usually included under the hydrogen type. It forms a subtype which comprehends the chlorides, fluorides, bromides, iodides, and cyanides, as well as the ethers of the hydracids, and the oxychlorides of the radicles of the monobasic acids; for example:—

Hydrochloric ether	$\left\{\begin{matrix}C_4H_5\\Cl\end{matrix}\right.$
Iodide of amyl	$\left\{\begin{matrix}C_{10}H_{11}\\I\end{matrix}\right.$
Benzoic oxychloride (chloride of benzoyl)	$\left\{\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right.$
Acetic oxychloride	$\left\{\begin{matrix}C_4H_3O_2\\Cl\end{matrix}\right.$

2. The type water . . . . $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$.

This series includes the oxides (comprising under this term acids, bases, and salts), sulphides, selenides, and tellurides, the alcohols, the hydrosulphuric ethers and mercaptans, the simple and compound ethers, the double ethers, the hydrated monobasic organic acids and their anhydrides: for instance,*

Wood spirit.	$\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O_2$
Alcohol	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2$
Hydrosulphuric ether	$\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}S_2$
Mercaptan	$\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2$

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* It will be seen, as we advance, that bodies are known which are formed upon the type of 2 molecules of water $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4$; such, for instance, as

Oil of vitriol	$\left.\begin{matrix}(S_2O_4)''\\H_2\end{matrix}\right\}O_4$
Oxalic acid	$\left.\begin{matrix}(C_4O_4)''\\H_2\end{matrix}\right\}O_4$
Glycol	$\left.\begin{matrix}(C_4H_4)''\\H_2\end{matrix}\right\}O_4$

whilst there are others formed upon the type of 3 molecules of water, $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_6$

Phosphoric acid	$\left.\begin{matrix}(PO_2)'''\\H_3\end{matrix}\right\}O_6$
Glycerin	$\left.\begin{matrix}(C_6H_5)'''\\H_3\end{matrix}\right\}O_6$

Ordinary ether . . . . $\begin{matrix}C_4H_5\\C_4H_5\end{matrix}$

Amylethylic ether . . . . . . $\begin{matrix}C_{10}H_{11}\\C_4H_5\end{matrix}$

Acetic ether . . . . $\begin{matrix}C_4H_3O\\C_4H_5\end{matrix}$

Hydrated acetic acid . . . . $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$

Acetic anhydride . . . . . . $\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2$

Hydrated oxide of ammonium . $\left.\begin{matrix}N\\ \end{matrix}\right\}O_2$

3. The ammonia type $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, includes the ni a phides, the com nd nias, and the amide

Ethylia (ethylamine) . . . . $\left\{\begin{matrix}C_4H_5\\H\\H\end{matrix}\right.$

Phosphodiethylia . . . . . . $\left\{\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}\right\}P$

Trimethylia (trimethylamine) . $\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N$

Acetamide . . . . $\left\{\begin{matrix}C_4H_3O_2\\H\\H\end{matrix}\right\}N$

Benzoyl-salicylamide . . . . $\left\{\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_4\\H\end{matrix}\right\}N$

Many compounds, not included under the preceding types, ay be referred to combinations of. two of the foregoing types ith each other.. Kekulé, for example, (*Lehrbuch der Org. hemie*, p. 124,) proposes to consider the amidated acids, such as he carbamic and the oxamic, as formed upon the combination of he type of ammonia and water:—

$$\left\{\begin{matrix}\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\\\left.\begin{matrix}H\\H\end{matrix}\right\}O_2\end{matrix}\right. \qquad \overbrace{\begin{matrix}\left.\begin{matrix}H\\H\\(C_2O_2)''\end{matrix}\right\}N\\\left.\begin{matrix}H\end{matrix}\right\}O_2\end{matrix}}^{\text{Carbamic acid.}} \qquad \overbrace{\begin{matrix}\left.\begin{matrix}H\\H\\(C_4O_4)''\end{matrix}\right\}N\\\left.\begin{matrix}H\end{matrix}\right\}O_2\end{matrix}}^{\text{Oxamic acid.}}$$

The tie between the two typical groups being in one case the dibasic radicle $(C_2O_2)''$, in the other $(C_4O_4)''$.

(922) *Theory of Polybasic Elements.*—The speculations of those who have followed up these ideas have led them to attribute the tendency of bodies to assume these typical forms of combination to special peculiarities in the nature of the elementary bodies themselves.

The more important of the elements have in accordance with these ideas been arranged in four principal groups, viz.:—

1. *Monatomic* or *monobasic* elements, one atom of which is in combination equivalent to H, or one atom of hydrogen.

2. *Diatomic* or *Dibasic* elements, one atom of which in combination is equivalent to H_2, or two atoms of hydrogen.

3. *Triatomic* or *Tribasic* elements, one atom of which is in combination equivalent to H_3, or three atoms of hydrogen.

4. *Tetratomic*, or *Tetrabasic* elements, each atom of which in combination is equivalent to H_4, or four atoms of hydrogen.

The particular class of the radicle may be pointed out as proposed by Odling, by affixing the marks ($''$) ($'''$) ($^{\text{iv}}$) to indicate its dibasic, tribasic, or tetrabasic character.

All the members of the same group exhibit a certain similarity in chemical characters; further, when any one of them enters into combination with any given element, *A*, the compound so formed is usually similar in atomic composition to the compounds which the other members of the group form with the same given element, *A*. For example:—

a. To the *monatomic* group are regarded as belonging—hydrogen, potassium, and the allied metals of the alkalies and alkaline earths, zinc, cadmium, and several other metals; as well as chlorine and the halogens.

Each of the monatomic elements combines with one atom of some other element of the same group; for instance:—

Hydrochloric acid	HCl
Iodide of potassium	KI
Bromide of zinc	ZnBr
Hydride of hydrogen (hydrogen gas) . .	HH

b. To the *diatomic* group the following elements are supposed to belong:—Oxygen ($\text{Ɵ}=16$), sulphur ($\text{S̶}=32$), selenium ($\text{S̶e}=79{\cdot}5$), and tellurium ($\text{Te}=129$).

One atom of each of these elements may unite with two atoms of the same monatomic element, or with one atom of two different monatomic elements; for example:—

Water	$\mathrm{HH\Theta}''$
Hydrosulphate of sulphide of potassium .	KHS''
Hydrate of lime	$\mathrm{CaH\Theta}''$

c. To the *triatomic* group belong nitrogen, phosphorus, arsenic, antimony, bismuth, and gold. One atom of each of these triatomic elements may combine with three atoms of an element of the monatomic group; as for instance:—

Ammonia	$\mathrm{H_3N}'''$
Terchloride of phosphorus	$\mathrm{P'''Cl_3}$
Teriodide of arsenic	$\mathrm{As'''I_3}$

d. To the *tetratomic* group some chemists suppose carbon (C = 12), and silicon (Si = 28) to belong.

The elements of this group unite with four atoms of the monatomic or with two of the diatomic group; for example:—

Marsh gas	$\mathrm{CH_4}$
Chloride of silicon	$\mathrm{SiCl_4}$
Carbonic acid	$\mathrm{C\Theta_2}$
Bisulphide of carbon	$\mathrm{CS_2}$
Silicic acid	$\mathrm{Si\Theta_2}$

From what has been just stated, it will be seen that it is assumed that no monatomic element can effect the union of other monatomic elements into a compound group of polybasic combining power.

Further, it is believed that complex groups or compound radicles exist which possess monobasic, dibasic, or polybasic power. No monobasic radicle has the power of effecting the union of two or more monobasic molecules into one polybasic radicle; but it is believed that just as each polybasic element can unite the atoms of several monobasic elements into one indivisible group, so also when a polybasic radicle enters into the composition of a body it may cause the union of several compound molecules of more or less simple constitution into one indivisible group or compound molecule; thus sulphuric acid may be regarded as formed upon the type of two molecules of water, the diatomic group $\mathrm{S\Theta_2}''$, forming the link which, by displacing two atoms of hydrogen, connects the two molecules together:—

$$\overbrace{\begin{array}{l}\left.\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\Theta\\ \left.\begin{array}{l}\mathrm{H}\\ \mathrm{H}\end{array}\right\}\Theta\end{array}}^{\text{Water.}} \qquad \overbrace{\begin{array}{l}\left.\begin{array}{r}\mathrm{H}\\ \mathrm{S\Theta_2}''\end{array}\right\}\Theta\\ \left.\begin{array}{r}\\ \mathrm{H}\end{array}\right\}\Theta\end{array}}^{\text{Oil of vitriol.}}$$

In like manner urea may be supposed to be formed upon the type of two molecules of ammonia, the diatomic group $\mathrm{C\Theta}''$ furnishing the link which connects the molecules into an indivisible whole:—

$$\begin{array}{l}\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}\\\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}\end{array}\quad;\quad\overbrace{\begin{array}{l}\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{C\Theta}''\end{matrix}\right\}\mathrm{N}\\\left.\begin{matrix}\phantom{\mathrm{H}}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}\end{array}}^{\text{Urea.}}$$

This principle, as will be seen hereafter, has been very extensively and ingeniously applied in explanation of the manner in which the compound atoms of many of the more complicated products of organic chemistry are held together in one indivisible group.*

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* Ingenious, however, as this view is, the arguments in its support are mainly derived from the compounds of carbon and hydrogen with each other, and with other bodies. It furnishes but a very incomplete explanation of many of the compounds of inorganic chemistry. For example, it gives no rational view of the constitution of the numerous and important class of the more complex metallic oxides. The same weight of a given metal combines with several different proportions of oxygen, occasioning the formation of sometimes as many as five distinct oxides, each combination with oxygen appearing, if the above theory be true, to indicate a separate atomic capacity in the metal. Such a series may be represented by the following general formulæ, in which M indicates the atom of any metal. The compounds of manganese, chromium, and iron, with oxygen, will serve as illustrations:—

(I.) M_2O_2	M_2O_3	M_2O_4	M_2O_6	M_2O_7
Mn_2O_2	Mn_2O_3	Mn_2O_4	Mn_2O_6	Mn_2O_7
Cr_2O_2	Cr_2O_3	Cr_2O_4	Cr_2O_6	Cr_2O_7
Fe_2O_2	Fe_2O_3		Fe_2O_6	

It is true that manganic anhydride (Mn_2O_6), ferric anhydride (Fe_2O_6), permanganic anhydride (Mn_2O_7), and perchromic anhydride (Cr_2O_7), are not known in their separate state, but chromic anhydride (Cr_2O_6) is well known; and the existence of manganate of potash (KO,MnO_3 or $KMnO_4$) and permanganate of potash (KO,Mn_2O_7 or KMn_2O_8) is not more easily explained on the theory of polybasic elements, than the occurrence of the anhydrides where they are known.

If R represent any electro-negative element, the following series may be obtained, which may be illustrated by the compounds of nitrogen, chlorine, and sulphur, with oxygen:—

R_2O_2	R_2O_4	R_2O_6	R_2O_8	R_2O_{10}	R_2O_{14}
N_2O_2	N_2O_4	N_2O_6	N_2O_8	N_2O_{10}	
Cl_2O_2		Cl_2O_6	Cl_2O_8	Cl_2O_{10}	Cl_2O_{14}
S_2O_2	S_2O_4	S_2O_6			

It must be admitted that the anhydrides of chloric and perchloric acids, as well as of hyposulphurous acid, are not known; but the chlorate (K,ClO_6 or

(923) *Causes of the Polybasic Character of Radicles.*—The study of polybasic compounds has been prosecuted with great activity and success within the last few years, and the circumstances under which an organic radicle exhibits a polybasic type have consequently attracted much attention: the present may afford a convenient opportunity for stating concisely the principal points which have been ascertained regarding this interesting subject, particularly respecting the radicles which contain carbon and hydrogen.

A large number of the hydrocarbon radicles which have at present been studied are monatomic, others are diatomic, and a few triatomic. The constitution of these compounds in certain cases enables us to anticipate what their powers will be.

1. A radicle of the form $C_{2n}H_{2n+1}$ such as methyl (C_2H_3), ethyl (C_4H_5), or amyl ($C_{10}H_{11}$), is invariably *monobasic;* as in chloride of ethyl $(C_4H_5)Cl$, and iodide of amyl $(C_{10}H_{11})I$; and ethylide of ethyl (C_4H_5) (C_4H_5).

2. A radicle of the form $C_{2n}H_{2n}$ such as ethylene (C_4H_4), tritylene (C_6H_6), octylene ($C_{16}H_{16}$), is *dibasic,* as in Dutch liquid $(C_4H_4)''Cl_2$.

3. A radicle of the form $C_{2n}H_{2n-1}$ may be either *tribasic* or *monobasic;* (C_6H_5), for example, is tribasic in glycerin, $\left.\begin{matrix}(C_6H_5)'''\\ H_3\end{matrix}\right\}O_6$, and monobasic in allylic alcohol $\left.\begin{matrix}C_6H_5\\ H\end{matrix}\right\}O_2$, and in chloride of allyl C_6H_5Cl; a radicle may sometimes be made to change its atomicity or basic power by the removal of hydrogen. As an example of this, we may take marsh gas, which is usually regarded as a neutral body of the methyl series: by acting upon this gas with chlorine, one, three, and four atoms of hydrogen may be removed in succession, and a corresponding number of atoms of chlorine substituted:—

Marsh gas (hydride of methyl) . . .	C_2H_4
Chloride of methyl	C_2H_3Cl
Iodide of methylene	$C_2H_2I_2$
Chloroform	C_2HCl_3
Bichloride of carbon	C_2Cl_4

KO,ClO_5) and perchlorate ($KClO_8$ or KO,ClO_7) of potash, and hyposulphite of baryta (BaO,S_2O_2,HO or BaS_2HO_4) are well known, and their constitution is equally incompatible with the theory of specific polybasic elements.

Again, cases occur in which, as in the terchloride of iodine ICl_3, an element such as iodine, reputed to be monatomic, combines with 3 atoms of another monatomic element, chlorine. For all these cases the theory of polyatomic elements gives no adequate explanation.

The third term in the series is not known with chlorine, but it has been obtained with iodine by Butlerow.

Now from these substitution-products of marsh gas, compounds of four different basic powers have been obtained, corresponding to the following different radicles, viz. :—

Monobasic . . .	C_2H_3	or	$C_{2n}H_{2n+1}$
Dibasic	C_2H_2	or	$C_{2n}H_{2n}$
Tribasic	C_2H	or	$C_{2n}H_{2n-1}$
Tetrabasic . . .	C_2	or	$C_{2n}H_{2n-2}$

The compound $(C_2H_3)Cl$ is manifestly a chloride of a monobasic radicle. If iodide of methylene be treated with acetate of silver, binacetate of methylglycol, the ether of a dibasic alcohol is procured (1045) :—

$$\overbrace{\left.\begin{matrix}(C_2H_2)''\\ I_2\end{matrix}\right\}}^{\text{Iodide of Methylene.}} + 2\,\overbrace{\left(\left.\begin{matrix}(C_4H_3O_2)\\ Ag\end{matrix}\right\}O_2\right)}^{\text{Acetate Silver.}} = 2\left(\left.\begin{matrix}Ag\\ I\end{matrix}\right\}\right) + \overbrace{\left.\begin{matrix}(C_4H_3O_2)_2\\ (C_2H_2)''\end{matrix}\right\}O_4}^{\text{Binacetate of Methylglycol.}};$$

and if chloroform be treated with sodium alcohol, a tribasic formic ether is obtained :—

$$\overbrace{\left.\begin{matrix}(C_2H)'''\\ Cl_3\end{matrix}\right\}}^{\text{Chloroform.}} + 3\,\overbrace{\left(\left.\begin{matrix}C_4H_5\\ Na\end{matrix}\right\}O_2\right)}^{\text{Sodium Alcohol.}} = 3\left(\left.\begin{matrix}Na\\ Cl\end{matrix}\right\}\right) + \overbrace{\left.\begin{matrix}(C_4H_5)_3\\ (C_2H)'''\end{matrix}\right\}O_6}^{\text{Triformic Ether.}};$$

Whilst, finally, if the bichloride of carbon be acted upon by aniline, a base is obtained containing $C_{38}H_{17}N_3$:—

$$\left.\begin{matrix}C_2{}^{\text{iv}}\\ Cl_4\end{matrix}\right\} + 3\left(\left.\begin{matrix}C_{12}H_5\\ H_2\end{matrix}\right\}N\right) = 4\left(\left.\begin{matrix}H\\ Cl\end{matrix}\right\}\right) + \left.\begin{matrix}C_2{}^{\text{iv}}\\ (C_{12}H_5)_3\\ H_2\end{matrix}\right\}N_3.$$

For the further prosecution of these speculations the reader may consult Kekulé (*Org. Chemie*, pp. 158—183).

(924) *Influence of Arrangement of Atoms in a Compound on its Properties.*—It is needful to bear in mind that a body does not necessarily belong to a given type merely because it may contain one of the characteristic elements which contribute to form the typical compound. It would be wrong, for example, to infer that a compound was formed on the hydrochloric acid type simply in consequence of the presence of chlorine among its components; since the properties of a body are dependent not only upon the nature and number of atoms of its component elements, but also in a very important manner upon the molecular arrangement of those components. Indeed, in many cases, the arrangement of the atoms in the compound has a greater influence upon its properties than even the nature of the elements of which it is composed. It may in fact be said that the whole theory of types is founded upon

the dissimilar behaviour of atoms otherwise identical save in their relative position in the molecule of the compound:—For example, the chlorine in chlorate of potash does not perform the same part that it does in chloride of potassium; in the latter instance it is susceptible of displacement when mixed with nitrate of silver; the soluble nitrate of potash and insoluble chloride of silver being formed when solutions of the two salts are mixed—

$$Ag,NO_6+KCl=K,NO_6+AgCl$$

whereas, when chlorate of potash and nitrate of silver are mixed, no precipitation of chloride of silver takes place. So it is in organic substances: for example, when isatin $C_{16}H_5NO_4$ (a compound derived from indigo) is distilled with hydrate of potash, a powerful volatile base termed aniline ($C_{12}H_5,H_2N$) is obtained. Now derivatives of isatin may be formed in which one, two, and three atoms of chlorine may be successively substituted in each molecule of isatin for an equal number of atoms of hydrogen; and when these chlorinated compounds are distilled with hydrate of potash, they yield substances corresponding in composition to aniline, but in which a certain number of atoms of hydrogen are displaced by a corresponding number of atoms of chlorine, thus:—

$$\overbrace{(C_{16}H_5)NO_4}^{\text{Isatin.}}+4\,\overbrace{(KO,HO)}^{\text{Hyd. Potash.}}=\overbrace{(C_{12}H_5)H_2N}^{\text{Aniline.}}+2\,\overbrace{(KO,C_2O_4)}^{\text{Carb. Potash.}}+H_2$$

$$\overbrace{(C_{16}H_4Cl)NO_4}^{\text{Chlorisatin.}}+4\,(KO,HO)=\overbrace{(C_{12}H_4Cl)H_2N}^{\text{Chloraniline.}}+2\,(KO,C_2O_4)+H_2$$

$$\overbrace{(C_{16}H_3Cl_2)NO_4}^{\text{Dichlorisatin.}}+4\,(KO,HO)=\overbrace{(C_{12}H_3Cl_2)H_2N}^{\text{Dichloraniline.}}+2\,(KO,C_2O_4)+H_2.$$

By the action of chlorine upon aniline another compound has been obtained termed trichloraniline ($C_{12}H_2Cl_3,H_2N$) in which three atoms of chlorine have taken the place of three atoms of hydrogen in the molecule of aniline.

It is particularly to be remarked that the basic properties of the aniline are preserved in these compounds, though with gradually decreasing distinctness; and it is not until the third atom of chlorine has been introduced, that the basic power finally disappears: thus aniline is powerfully basic; chloraniline is distinctly basic; dichloraniline, feebly so; and trichloraniline is neutral.

Not one of these bodies when in solution, combined with nitric or sulphuric acid for instance, gives any precipitate of chloride when mixed with nitrate of silver; yet a single equivalent of chlorine, in the form of hydrochloric acid, will neutralize the basic power of any of these compounds: thus if hydrochloric acid be combined with aniline so as to form hydrochlorate of this base ($C_{12}H_7N,HCl$), the solution will have all the characters of a neutral salt, and will occasion an immediate precipitate when its solution is mixed with one of nitrate of silver;

$$\overbrace{C_{12}H_7N,HCl}^{\text{Hydrochlor. of Aniline.}}+\overbrace{AgNO_6}^{\text{Nitrate of Silver.}}=\overbrace{AgCl}^{\text{Chloride of Silver.}}+\overbrace{C_{12}H_7N,HNO_6}^{\text{Nitrate of Aniline.}}.$$

These differences may be accounted for upon the supposition that chlorine, when in combination, may discharge different functions; thus it is assumed that in the different chlorinated anilines the chlorine has entered more intimately into the composition of the body than in the case just cited, since it is supposed that part of the hydrogen in the molecule of the base has been actually displaced by chlorine in the first cases; whereas, in the last, the chlorine is external to the base. The full importance of such processes of substitution will be made manifest as the reader proceeds: and in order to facilitate the acquirement of distinct notions upon this point, we pass next to the consideration of the principal modes in which the chemist effects the metamorphoses of the compounds which come before him.

§ III. Production of Chemical Metamorphoses.

(925) Three principal methods are employed in examining the chemical composition of organic bodies, and in tracing their relations to other compounds. These three methods are—1. That of *oxidation*. 2. That of *reduction*. 3. That of *substitution*, including double decomposition.

1. *Oxidation*.—It will be unnecessary to consider minutely the effects of rapid direct oxidation or combustion, as the general result in all cases where a sufficient amount of air is supplied, is to convert the carbon into carbonic acid, and the hydrogen into water, whilst the nitrogen is commonly liberated in the free state. It is the study of the process of gradual oxidation which affords results so instructive to the chemist. When an organic body is placed in contact with a powerful oxidizing agent, such as nitric acid, chromic acid, or a mixture of sulphuric acid and black oxide of manganese, the effects which are produced will vary in different cases. In some compounds hydrogen alone will be oxidized, as when alcohol is submitted to distillation with chromic acid; in which case water is produced, and a new body, aldehyd, containing all the carbon of the alcohol, is produced:—

$$2\,\overbrace{C_4H_6O_2}^{\text{Alcohol.}} + O_4 = 2\,\overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\,H_2O_2.$$

In other instances, both the carbon and the hydrogen are partially removed in the form of carbonic acid and water, whilst an organic body of less complex composition is left; as when stearic acid is treated with nitric acid: in this case the products vary with the strength of the acid employed, and with the time during which they are left to act upon each other; so that the following compounds, each successively simpler in composition, might be obtained from stearic acid ($C_{36}H_{36}O_4$):—

Capric acid . .	$C_{20}H_{20}O_4$	Adipic acid . .	$C_{12}H_{10}O_8$
Suberic acid .	$C_{16}H_{14}O_8$	Succinic acid .	$C_8\,H_6\,O_8$
Pimelic acid .	$C_{14}H_{12}O_8$	Butyric acid .	$C_8\,H_8\,O_4$
Œnanthylic acid	$C_{14}H_{14}O_4$	&c.	

But it is not only to the processes of oxidation effected in the laboratory that it is necessary to attend. Oxidizing actions are in constant operation unperceived on every side of us. The gradual decay of organic compounds is owing to their spontaneous slow oxidation: for decay is, in reality, only a slow process of combustion; a fact which Liebig indicates by substituting the term *eremacausis* for that of decay (from ἤρεμος 'gentle,' καῦσις 'combustion'). The decay of wood is a familiar instance of this kind; the hydrogen of the wood becomes more rapidly oxidized than its carbon, and the result is the formation of a brown powder termed ulmin or humus, in which the carbon preponderates over the hydrogen and the oxygen to a much greater extent than in the wood from which it was formed. Such actions take place generally under the combined influence of moisture and of a temperature of about 60° or upwards. If the substance be perfectly dry, or if the temperature fall to the freezing point, oxidation is usually completely arrested. Contact with a body which is itself actively undergoing slow oxidation will frequently induce this oxidizing action in substances which have a strong affinity for oxygen, but which do not, when in a pure state themselves undergo oxidation. Alcohol, for example, does not undergo oxidation when allowed to evaporate in air; but if it be mixed with a little must or some substance susceptible of oxidation, the alcohol, when brought into contact with atmospheric air, becomes oxidized, and furnishes aldehyd and acetic acid (1078). Sometimes the steps of the process may be pretty clearly traced; for example, a solution of grape sugar in an alcoholic solution of potash does not absorb oxygen when exposed to the air; but the addition of a minute quantity of sulphindylic acid (1324) effects the oxidation of the sugar; probably, as Traube suggests, by the absorption of oxygen on the part of the sulphindylic acid, and the transfer of oxygen to the sugar; the sulphindylic acid absorbing fresh oxygen and again parting with it to fresh portions of sugar, acting in fact as a carrier of oxygen, just as deutoxide of nitrogen does to sulphurous acid, during the manufacture of oil of vitriol (344). Another analogous experiment of Traube's consists in heating a solution of oxide of copper containing a large quantity of hydrochlorate of ammonia, with grape sugar; no reduction takes place even when the liquid is boiled; but if a small quantity of reduced and colourless sulphindylic acid be added, the blue colour of the indigo reappears, owing to the absorption of oxygen by the indigo acid from the black oxide of copper; the acid then gives up its oxygen to the sugar, after which it again takes up more oxygen from a fresh quantity of oxide of copper; so that in a short time the whole of the sugar is oxidized, and the oxide of copper reduced to the suboxide, whilst the sulphindylic acid is left apparently unaltered. The sulphindylic acid is in fact much more easily reduced than the oxide of copper, and yet it has the power of easily absorbing oxygen from this oxide. An action similar to this of the sulphindylic acid in favouring oxidation in the sugar is supposed to exist in many other cases, as for example in the ordinary process of vinegar-making from sugar and water, where the presence of certain oxidizable matters is found by experience to be necessary.

These slow processes of combustion are intimately connected with the development of ozone, or chemically active oxygen (288). In certain cases the formation of ozone is so abundant during such actions, that they furnish some of the best means of obtaining this singular body. Thus ozone is always formed during the slow oxidation of phosphorus in air; and it appears also to be produced in the oxidation of oil of turpentine and of ether under particular circumstances, as when a hot platinum wire is suspended in a mixture of the vapour of ether and atmospheric air. The ozone thus developed has in its turn a powerful influence in promoting the oxidation of the organic body, though of course it cannot be supposed that the presence of ozone is essential to the production and development of such oxidations, for they constantly occur where no ozone can be supposed to exist; whilst in other cases the production of ozone appears to be a consequence rather than a cause of the process.

The importance of studying the action of such cases of oxidation must be obvious, when it is borne in mind that it is always by the agency of oxygen that the various complex substances contained in the animal body are gradually resolved into carbonic acid, water, and ammonia; in one or other of which forms the organic products return again to the domain of inorganic chemistry.

(926) 2. *Metamorphoses by Reduction.*—Processes of reduction are less completely under the control of the chemist than those of oxidation, and they are consequently not applied in the laboratory so easily or so frequently. In a few cases one or two atoms of hydrogen may be combined with each molecule of the original compound; thus alloxan, under the influence of sulphuretted hydrogen, furnishes alloxantin:—

$$4\,\overbrace{C_8H_4N_2O_{10}}^{\text{Alloxan.}}+2\,H_2S_2=2\,\overbrace{C_{16}H_{10}N_4O_{20}}^{\text{Alloxantin.}}+S_4;$$

and in a somewhat similar manner blue indigo, under the combined action of protoxide of iron and alkalies, becomes converted into white indigo:—

$$2\,\overbrace{C_{16}H_5NO_2}^{\text{Blue Indigo.}}+H_2O_2+2\,Fe_2O_2=2\,\overbrace{C_{16}H_6NO_2}^{\text{White Indigo.}}+2\,Fe_2O_3.$$

Sometimes deoxidation occurs during the process of fermentation; as when malate of lime is allowed to ferment in contact with decayed cheese; succinic, acetic, and carbonic acids being the result: the formula of malic acid differing from that of succinic acid by containing more oxygen in the proportion of O_2.

Malic acid . = $C_8H_6O_{10}$
Succinic acid . = $C_8H_6O_8$

(927) 3. *Metamorphoses by Substitution.*—The method to be adopted in the formation of new compounds by displacement or substitution, constitutes an important object of chemical inquiry, and the prosecution of such researches often gives a clue to the molecular constitution of the body under examination, and to its relations to other compounds. The ordinary method of preparing insoluble inorganic compounds by double decomposition, is simply a case of the substitution of one base or one acid for another: when solutions such as those of carbonate of potash and nitrate of baryta are mingled, the barium is exchanged for potassium, and reciprocally potassium for barium; $2\,KO,C_2O_4+2(BaO,NO_5)=2\,BaO,C_2O_4+2(KO,NO_5)$. This species of substitution is also a familiar operation amongst the compounds of organic chemistry;

for the chemist has learned to displace* various elementary sub- stances by compound groups, as when by the mutual action o hydrocyanic acid and red oxide of mercury, cyanide of mercur and water are produced; $2\,HCy+Hg_2O_2=2\,HgCy+H_2O_2$: th hydrogen and the mercury being substituted the one for th other; whilst the group Cy ($=C_2N$), takes the place of the oxyge in the oxide of mercury. Substitutions of groups of greater com plication than these are also readily effected, and it is even possibl in some instances to produce true organic compounds from in organic elements (930).

Few instances of substitution are more remarkable than thos by which ammonia may be converted into a complex organi base:—when bromide of ethyl, for example, is mixed with a solu tion of ammonia in alcohol, placed in a sealed tube and heate for a few hours to 212°, a reaction occurs, in consequence o which, as the mixture cools, crystals of hydrobromate of ethyli (C_4H_7N,HBr) are produced; and if this compound be distille with hydrate of potash, bromide of potassium, water, and a ne base, ethylia (C_4H_7N), will be formed.

Now, the molecule of ammonia may be represented as con sisting of

$$\left.\begin{array}{l}H\\H\\H\end{array}\right\}N;\quad\text{and the molecule of ethylia may in like manner be viewed as}=\quad\left.\begin{array}{c}C_4H_5\\H\\H\end{array}\right\}N,$$

or as ammonia in which 1 atom of hydrogen has been displac by C_4H_5, or its equivalent of ethyl. The substitution will understood from the following equations:—

$$\overbrace{C_4H_5Br}^{\text{Bromide of Ethyl.}}+H_3N=\overbrace{C_4H_5,H_2N,HBr}^{\text{Hydrobromate of Ethylia.}};\ \text{and}$$

$$\overbrace{C_4H_5,H_2N,HBr}^{\text{Hydrobromate of Ethylia.}}+KO,HO=\overbrace{C_4H_5,H_2N}^{\text{Ethylia.}},+KBr+H_2O_2.$$

Again, if bromide of ethyl be heated similarly with this ne base, a second atom of hydrogen may be displaced, and a hyd bromate of a second more complicated base, diethylia, (C_8H_{11} will be obtained; and from this hydrobromate the pure bas liberated by distillation with hydrate of potash. In diethylia t atoms of hydrogen have been displaced by ethyl:—

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* The French term *remplacement* is usually but inaccurately rend *replacement*; the true meaning of the latter word is putting back into place, and not *displacement*, which conveys the meaning of the French w more accurately.

$$\text{Thus, diethylia, } C_8H_{11}N, = \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ H \end{matrix}\right\} N\,;$$

and, again, if bromide of ethyl be made to act upon diethylia, the third atom of hydrogen is displaced, and triethylia ($C_{12}H_{15}N$) in combination with hydrobromic acid is produced; and thus a complex ammonia $\left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} N$, is built up step by step, by the successive removal of hydrogen and the substitution of a corresponding number of equivalents of ethyl. Many cases of the same nature will be exhibited when the artificial formation of organic bases comes under the notice of the reader (1183).

(928) *Substitution of Chlorine and its Analogues for Hydrogen.*—Other remarkable species of compounds which are obtained by substitution, are those in which a portion of the hydrogen of the original body is displaced by chlorine. When a current of dry chlorine gas is passed through certain organic liquids containing hydrogen, the chlorine is rapidly absorbed, especially if the action be aided by exposure to light or to the direct rays of the sun; the organic compound undergoes decomposition, abundance of hydrochloric acid escapes, and a new organic body, into the composition of which chlorine enters, is formed. This decomposition is usually very definite in its nature. In the majority of cases the new product is perfectly analogous to the compound from which it is furnished, and contains the same number of elementary atoms, but a certain number of atoms of its hydrogen has been displaced by a corresponding number of equivalents of chlorine; so that for every atom of hydrogen removed in the form of hydrochloric acid, an equivalent of chlorine has been substituted. This very singular species of substitution was originally observed by Gay Lussac to take place when wax is acted upon by chlorine; and a good example of its occurrence has already been considered, when engaged in tracing the conversion of Dutch liquid into sesquichloride of carbon (400). This kind of substitution is of frequent occurrence, and some of the most instructive instances are afforded by the action of chlorine upon ether and upon other derivatives of alcohol. For example, when the vapour of hydrochloric ether (C_4H_5Cl) is subjected to the action of chlorine in the direct rays of the sun, the chlorine immediately begins to act upon the ether, and the action may then be continued in diffused daylight. The experiment may be conducted in an apparatus similar to that used in preparing Dutch liquid, and

shown in fig. 295, part ii. p. 247. In order to supply th chloric ether, a mixture of hydrochloric acid and alcohol i in the retort *a*, and warm water substituted for sulphuric the bottle *c*. By attention to a number of precautions, a su of compounds is furnished, in which, equivalent for equiva hydrogen is displaced by chlorine, until at length the last obtained is sesquichloride of carbon. The following table the successive steps of the reaction, and indicates some of perties of the different compounds:—

Name of Compound.	Formula.	Boiling Point °F.	Specific
			Liquid.
Hydrochloric ether . . .	C_4H_5Cl	52°	0·874
Chlorinated ditto	$\left.\begin{matrix}C_4H_4Cl\\Cl\end{matrix}\right\}$	147°	1·174
Dichlorinated ditto	$\left.\begin{matrix}C_4H_3Cl\\Cl_2\end{matrix}\right\}$	171°	1·372
Trichlorinated ditto . . .	$\left.\begin{matrix}C_4H_2Cl\\Cl_3\end{matrix}\right\}$	215°	1·530
Tetrachlorinated ditto . . .	$\left.\begin{matrix}C_4H\,Cl\\Cl_4\end{matrix}\right\}$	295°	1·644
Sesquichloride of carbon . .	C_4Cl_5Cl	360°	2·4

The density of these compounds, both in the state of liqui vapour, increases as the quantity of chlorine increases; the of 1 molecule of vapour is the same for all, being = 4 w volume of O = 8 is taken as 1. It will also be seen that ing point rises as the quantity of chlorine increases. molecule of each of these bodies contains the same nu elementary atoms, which appear to be grouped in the sam in each compound. The chlorine appears to have taken t of hydrogen in the group without disturbing the relative of the other elements which enter into its formation—ju brick in an edifice may be conceived to admit of being r whilst its place is supplied by a block of wood or of stone, altering the form or symmetry of the building.

A striking proof of the persistence of the molecular arra of the compound, and of the preservation of the relative col of its component particles, is afforded when two parallel isomeric substitution-compounds are compared with eac Such a parallel is afforded by the chlorinated compounds from hydrochloric ether and from Dutch liquid.

It has already been explained (400), that when equal of gaseous chlorine and olefiant gas are mixed together, t dually enter into combination, and form the oily fragrant body known as Dutch liquid ($C_4H_4Cl_2$): and further, that when this liquid is submitted to the action of chlorine in excess, a series of compounds is obtained from it, in which each atom of hydrogen in succession is displaced by an equivalent of chlorine. Now it will be found, on comparing these bodies with those furnished by acting upon hydrochloric ether, that a certain number of them are metameric in pairs, although the two members of each pair possess very different properties, as may be seen by examining the following table, where the metameric pairs are placed side by side :—

Name of Compound.	Formula.	Boiling Point °F.	Specific Gravity.	
			Liquid.	Vapour.
Dutch liquid	C_4H_3Cl,HCl	184°	1·280	3·450
Monochlorinated hydrochloric ether	C_4H_4Cl,Cl	147°	1·174	3·478
Monochlorinated Dutch liquid	$C_4H_2Cl_2,HCl$	239°	1·422	4·613
Dichlorinated HCl ether . .	$C_4H_3Cl_2,Cl$	171°	1·372	4·530
Dichlorinated Dutch liquid . .	C_4HCl_3,HCl	275°	1·576	5·767
Trichlorinated HCl ether . .	$C_4H_2Cl_3,Cl$	215°	1·530	5·799
Trichlorinated Dutch liquid .	C_4Cl_4,HCl	307°	1·663	
Tetrachlorinated HCl ether .	C_4HCl_4,Cl	295°	1·644	6·975
Sesquichloride of carbon . .	C_4Cl_4,Cl_2(?)	356°	Solid.	8·157
Sesquichloride of carbon . .	C_4Cl_5,Cl (?)		2·40	

A molecule of each of these compounds in the gaseous state occupies four volumes of vapour ; consequently the vapour densities of each metameric pair nearly coincide ; indeed it is a necessary condition, that equal weights of all metameric bodies yield equal volumes of vapour, and therefore, allowing for errors of experiment, metamerides must always coincide in density in the gaseous state : but in the liquid form, the densities of the components of each pair are widely different, and the temperatures at which they boil are also different. There is likewise a marked difference in their chemical properties, and in the mode of their decomposition. The following are some of the points of difference :—The substitution compounds derived from hydrochloric ether are scarcely affected even when boiled with an alcoholic solution of potash, or with one of hydrosulphate of potassium (KS, HS) ; and potassium may remain in them at ordinary temperatures without being acted upon. On the other hand, when the compounds derived from Dutch liquid are treated with an alcoholic solution of potash, they are rapidly decomposed, chloride of potassium and water are formed, and a new substance, considerably more volatile than the original chlorinated compound is obtained: thus:—

$$\overbrace{C_4H_3Cl,HCl}^{\text{Dutch Liquid.}}+KO,HO = C_4H_3Cl+KCl+H_2O_2.$$

By the action of Hydrate of Potash			New Compounds.	Boiling Point ° F.	Sp. gr. of Liquid.
Dutch liquid . . .	C_4H_3Cl, HCl	yields	C_4H_3Cl	14°	
Monochlorinated ditto	$C_4H_2Cl_2,HCl$	„	$C_4H_2Cl_2$	95°	1·250
Dichlorinated ditto .	$C_4H\ Cl_3,HCl$	„	$C_4H\ Cl_3$		
Trichlorinated ditto .	$C_4\ \ Cl_4,HCl$	„	$C_4\ \ Cl_4$	251·6°	1·619

If an alcoholic solution of hydrosulphate of potassium be employed instead of the hydrated alkali, various sulphuretted compounds are produced; and the chlorinated derivatives of Dutch liquid are violently decomposed by potassium.

Now it is obvious that the original difference of molecular grouping is preserved throughout, both in the series of Dutch liquid and in that of hydrochloric ether, so that the chemist is thus, as it were, enabled to dissect these compounds by the agency of chlorine; and it is not until the last atom of hydrogen is removed, that the molecular arrangement breaks down; both groups in that case yielding the same compound—viz., the sesquichloride of carbon.

The discovery that the substitution of chlorine for hydrogen was practicable, at first excited the greatest astonishment amongst chemists, since owing to the powerful affinities of chlorine, particularly when its electrical opposition to hydrogen is borne in mind, the possibility of such an occurrence was never suspected. The displacement of oxygen by chlorine was familiar to the mind of the chemist, but the displacement of hydrogen by chlorine was a circumstance in opposition to the doctrines of affinity then prevalent. The discovery of this remarkable fact has led to the production by substitution of an immense number of analogous compounds in other groups of organic bodies. The new products so obtained, however, are in general possessed of but little intrinsic interest. The importance of accurately studying the steps by which these substitutions are effected, can, however, be scarcely over-estimated, owing to the light which they frequently throw upon the views of the composition of organic compounds, and of their relations to others where no obvious connexion had been previously traced.

It seldom happens that the process of substitution can be followed through its successive stages so completely as in the case of hydrochloric ether or of Dutch liquid; the products of the operation are mingled with each other, and often cannot be satisfactorily separated. The first atoms of hydrogen are displaced more readily than the others, and frequently the last atom is removed with great difficulty. It is often necessary at first to moderate the action by cooling the liquid artificially, and by placing it either in obscurity or only in the diffused light of day; whilst to complete the displacement of the last portions, the strongest sunlight, aided by a temperature of ebullition, is frequently requisite.

Substitutions of bromine and iodine for hydrogen may also be effected by analogous methods, although, owing to the feebler affinities of these elements, the reactions take place with less vehemence.

In a few instances a substitution of an atom of deutoxide of nitrogen (NO_2) for an atom of hydrogen has been observed; thus dinitronaphthalin, by the reducing action of sulphuretted hydrogen, yields a compound termed nitrosonaphthylamine, or ninaphthylia—

$$\overbrace{C_{20}H_6(NO_4)_2}^{\text{Dinitronaphthalin.}} + 4\,H_2S_2 = \overbrace{C_{20}H_8(NO_2)N}^{\text{Ninaphthylia.}} + 3\,H_2O_2 + 2\,S_4.$$

In other instances peroxide of nitrogen (NO_4)* may be substituted for hydrogen, equivalent for equivalent, as when benzol ($C_{12}H_6$) is acted upon by nitric acid, and is converted into nitrobenzol ($C_{12}H_5\,NO_4$) whilst water is formed. Each atom of nitric acid (HO,NO_5) in these cases loses oxygen in the proportion of O_2, half of this oxygen combines with the basic hydrogen of the acid, the other half combines with an atom of hydrogen derived from the benzol, whilst an equivalent of peroxide of nitrogen takes the place of the hydrogen so removed; thus:—

$$\overbrace{\left.\begin{matrix}C_{12}H_5\\ H\end{matrix}\right\}}^{\text{Benzol.}} + \overbrace{\left.\begin{matrix}NO_4\\ H\end{matrix}\right\}O_2}^{\text{Nitric acid.}} = \overbrace{\left.\begin{matrix}C_{12}H_5\\ NO_4\end{matrix}\right\}}^{\text{Nitro-benzol.}} + \left.\begin{matrix}H\\ H\end{matrix}\right\}O_2.$$

Schutzenberger (*Comptes Rendus*, lii. 135) appears to have succeeded, in some cases, in effecting the indirect substitution of electro-negative bodies, such as chlorine, iodine, and cyanogen, for even the *basic* hydrogen of certain organic acids; and thus, in a certain sense, chlorine and its analogues are shown to be chemically equivalent to potassium. In order to effect these transformations it is necessary to displace the hydrogen of the acid, or the metal which occupies its place, by some electro-negative group. Thus, if acetate of potash be treated with chloride of acetyl (1094) acetic anhydride is obtained :—

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* It is worthy of notice that 1 atom of peroxide of nitrogen (NO_4) in the gaseous state occupies 4 volumes, whilst the equivalent of hydrogen, of chlorine, and of other elements which admit of being substituted for each other, occupies 2 volumes.

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\K\end{matrix}\right\}O_2}^{\text{Acetate of potash.}}+\overbrace{\left.\begin{matrix}C_4H_3O_2\\Cl\end{matrix}\right\}}^{\text{Chloride of acetyl.}}=\overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2}^{\text{Acetic anhydride.}}+KCl;$$

and if acetic anhydride (1108) be digested at a very low temperature with hypochlorous anhydride, the red-coloured liquid at first obtained gradually becomes colourless, and an acetate of chlorine is formed :—

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2}^{\text{Acetic anhydride.}}+\overbrace{\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O_2}^{\text{Hypo-chlorous anhydride.}}=\overbrace{\left.\begin{matrix}C_4H_3O_2\\Cl\end{matrix}\right\}O_2}^{\text{Acetate of chlorine.}}+\overbrace{\left.\begin{matrix}C_4H_3O_2\\Cl\end{matrix}\right\}O_2}^{\text{Acetate of chlorine.}}.$$

Similar compounds may be obtained with bromine, with iodine, and with cyanogen. All these bodies are extremely unstable, most of them undergo gradual decomposition at common temperatures; the compound with bromine even explodes spontaneously, that with chlorine at 212°, and that with iodine at a temperature somewhat higher.

These compounds are respectively metameric with chloracetic (1110), bromacetic, and iodacetic acids, but they bear no resemblance to them in properties. Similar combinations with butyric and benzoic acids have been obtained.

(929) *Inverse Substitutions.*—A series of substitutions the reverse of those just described, and in which the chlorine or iodine is displaced by a corresponding number of equivalents of hydrogen, often furnishes results of very great interest; but the methods of effecting these inverse substitutions are only beginning to attract the notice which their importance demands. 1. Berthelot (*Ann. de Chimie,* III. li. 48) has pointed out that when the compounds for experiment are of a very stable character, *free hydrogen* at an elevated temperature may effect this species of substitution, though a good deal of the chlorinated compound is always destroyed: several of the chlorides of carbon yield such results; thus, protochloride of carbon when transmitted in vapour with hydrogen through a glass tube filled with fragments of pumice and heated to redness, furnishes hydrochloric acid and olefiant gas :—

$$C_4Cl_4+4\ H_2 = C_4H_4+4\ HCl.$$

Bichloride of carbon yields marsh gas and olefiant gas :—

$$C_2Cl_4+4\ H_2 = C_2H_4+4\ HCl.$$

The olefiant gas is the result of the effect of heat upon the bichloride of carbon which is partially decomposed into the protochloride (C_4Cl_4) and free chlorine, and this protochloride is then converted into olefiant gas by the action of the hydrogen, as already explained.

2. *Nascent hydrogen* may sometimes be more advantageously resorted to in effecting reductions of this description. In this way Melsens, by acting upon trichloracetic acid with an amalgam of potassium, reproduced acetic acid; Frankland, by means of zinc, has obtained the hydrocarbon radicles of the alcohols and their hydrides (1038, 1041) from their iodides; and Berthelot, by enclosing the bromide of ethylene, of tritylene, of tetrylene, and of amylene in strong glass tubes in contact with water, copper foil, and iodide of potassium, and subsequently heating the mixture to 527° in an oil bath, procured olefiant gas, tritylene, tetrylene, and amylene, accompanied by some gaseous bodies which are products of a secondary decomposition. If the use of copper be omitted, the products of secondary decomposition are more considerable; so that it would appear that a part of the organic body had taken the place of the copper, and had undergone oxidation at the expense of the oxygen of the water, whilst the hydrogen had effected an inverse substitution and formed *hydrides* of ethylene, tritylene, tetrylene, and amylene.

When the copper is present, the reaction is probably of the following nature:—

$$C_4H_4Br_2+H_2 = C_4H_4+2\ HBr.$$

And when the copper is not added, the decomposition may be represented as follows:—

$$C_4H_4Br_2+2\ H_2 = C_4H_4H_2+2\ HBr.$$

(930) *Synthetic Production of Organic Compounds.*—A combination of the operations of direct chemical action with those of substitution, enables the chemist in some instances to build up a truly organic compound from inorganic materials. This is well exemplified in the artificial production of acetic acid in the manner first pointed out by Kolbe (Liebig's *Annal.* liv. 186):—When carbon is heated to bright redness in the vapour of sulphur, combination between the two elements takes place, and bisulphide of carbon (C_2S_4) is formed. When bisulphide of carbon is digested for several days with aqua regia, a white volatile crystalline compound is obtained, which is insoluble in water, but soluble in alcohol and in ether: it melts at 275°, and at 338° it enters into

ebullition : it has a peculiar odour which brings tears into the eyes, and its vapour has a sp. gr. of 7·43. This substance, discovered by Berzelius and Marcet, has the composition represented by the formula $C_4Cl_8S_4O_8$ [$= 2\,(C_2Cl_4S_2O_4)$], and is termed by Kolbe *sulphite of perchloride of carbon.* When this compound is transmitted in vapour through a porcelain tube at a dull red heat, it is decomposed into the liquid protochloride of carbon (C_4Cl_4), sulphurous acid, and free chlorine :—

$$(C_4Cl_8S_4O_8) = C_4Cl_4 + 2\,Cl_2 + 2\,S_2O_4.$$

If the protochloride of carbon thus obtained be placed beneath a layer of water, and exposed to the sun's rays in a large vessel filled with chlorine gas, sesquichloride of carbon (C_4Cl_6) is formed abundantly, and at the same time an acid solution is obtained, which, after saturation with lime or with some other base, is found to contain a chloride and a trichloracetate of the base ; if lime be used, the formula of the salt is $CaO,\ C_4Cl_3O_3$. Kolbe attributes its production to the reaction of water upon sesquichloride of carbon at the moment of its formation, as shown by the following equation :—

$$\overbrace{C_4Cl_6}^{\text{Sesquichlor. carbon.}} + 2\,H_2O_2 = \overbrace{HO,C_4Cl_3O_3}^{\text{Trichloracetic acid.}} + 3\ HCl.$$

Now if trichloracetic acid be treated with an excess of potassium in the form of an amalgam, the chlorine is entirely withdrawn from this compound, and its place is supplied by hydrogen ; in other words, it is converted into acetic acid :—

$$\overbrace{HO,C_4Cl_3O_3}^{\text{Trichloracetic acid.}} + 3\ K_2 + 2\ H_2O_2 = \overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}} + 3\ KCl + 2\ (KO,HO).$$

Thus a complex organic acid is obtained from inorganic materials :— the successive steps of the operation being 1. bisulphide of carbon ; 2. sulphite of perchloride of carbon ; 3. protochloride of carbon ; 4. trichloracetic acid ; and 5. acetic acid.

The earliest and one of the most remarkable instances of the synthetic formation of an organic compound was afforded in the case of urea, which Wöhler discovered might be artificially obtained by the action of cyanic acid on ammonia ; for on attempting to evaporate a solution of cyanate of ammonia, this salt undergoes an isomeric transformation, and yields urea :—

$$\overbrace{H_4NO,\ C_2NO}^{\text{Cyanate of ammonia.}} = \overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

It has been well remarked by Berthelot (*Chimie Organique fondée sur la Synthèse*, Vol. I. p. 133), "In order to accomplish the reproduction of a natural compound, it is often necessary to erect an entire edifice founded upon the formation of artificial products. The examination of these enables us to ascertain the general laws which regulate the composition of compounds presented by nature, and the method by which their study, whether analytical, or synthetical, may be followed with some hope of a successful result." No experimenter has laboured so successfully in this field as the eminent chemist just quoted, who has indeed established new modes of investigation by his researches. Among many remarkable discoveries which he has made in this direction, is the method of obtaining formic acid synthetically by combining carbonic oxide with hydrate of potash (1104):—

$$C_2O_2 + KO,HO = \overbrace{KO,C_2HO_3}^{\text{Formiate of potash.}}.$$

He has likewise obtained olefiant gas by the reaction of copper and sulphuretted hydrogen upon bisulphide of carbon; and from olefiant gas he has procured alcohol. The same chemist has also, conjointly with De Luca, converted the hydrocarbon tritylene into glycerin, and he has further shown that glycerin may be transformed into one variety of sugar.

Strecker has likewise succeeded in obtaining taurin by synthesis, and there can be no doubt that as researches in this direction are multiplied, new methods of preparing bodies as yet obtainable only from the products of the living plant or animal, will be devised.

CHAPTER II.

THE SACCHARINE OR AMYLACEOUS GROUP.—VARIETIES OF FERMENTATION.

(931) The compounds which belong to the group to which the following chapter is mainly devoted, are among the most important and abundant constituents of plants. One of the most remarkable features of their chemical composition is the circumstance that they all contain oxygen and hydrogen exactly in the proportions requisite to form water, and hence they have by some writers been spoken of as *hydrates of carbon*. This term, however, is by no

means intended to signify that all the hydrogen and oxygen exi in them united in the form of water, but merely to indicate th the proportion of their components is such as might admit of the elements being so arranged. Owing to this peculiarity of comp sition, many of these bodies admit of being readily transformed o into the other by the addition or abstraction of the elements water, and several of them are especially prone to undergo t changes produced by fermentations of various kinds. In the pr sence of dehydrating agents, the sugars, lignin, and many bodies this class yield humus-like products. When submitted to oxid tion by the action of nitric acid, most of them yield oxalic aci and under the influence of a mixture of concentrated nitric a sulphuric acids, substitution compounds are obtained, in which portion of their hydrogen is displaced by peroxide of nitrog The most remarkable of these substitution compounds is pyroxyl (gun-cotton), the peculiar inflammability and explosive charact of which is well known; but all of the nitrous substitution pr ducts of this class partake more or less of the inflammable a explosive properties which are so signally exhibited by pyroxyli

The researches of Berthelot have rendered it probable that t sugars, as well as mannite and the bodies allied to it, are pol atomic alcohols like glycerin (1067), for he has found that th possess the power of entering into combination with various aci with elimination of water, in some cases yielding peculiar co gated acids, analogous to the tannic, and, in others, furnishi neutral bodies closely allied to the fats.

In the present chapter the compounds mentioned in the follo ing table will be described. In a few of the substances enumerat in the lower part of the table, the proportion of oxygen and hyd gen differs from that of the sugars and starches.

*Amylaceous and saccharine group.**

Cane sugar (sucrose) . . .	$C_{12}H_{11}O_{11}$
Mycose	$C_{12}H_{11}O_{11}+2\ Aq$
Trehalose	$C_{12}H_{11}O_{11}+2\ Aq$
Melezitose	$C_{12}H_{11}O_{11}+x\ Aq$
Fruit sugar (fructose) . . .	$C_{12}H_{12}O_{12}$
Starch sugar (glucose) . . .	$C_{12}H_{12}O_{12}+2\ Aq$
Milk sugar (lactose) . . .	$C_{24}H_{19}O_{19}+5\ Aq$

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* Some chemists double the formulæ of several of these bodies, and rep sent most of the substances included in the upper division of the table containing C_{24}, cane sugar being $C_{24}H_{22}O_{22}$. The formulæ of mannite and pinite were formerly given as half that contained in the table.

Melitose	$C_{24}H_{24}O_{24}+4\,Aq$
Eucalyn	$C_{12}H_{12}O_{12}+2\,Aq$
Sorbin	$C_{12}H_{12}O_{12}$
Inosin (inosite)	$C_{12}H_{12}O_{12}+4\,Aq$
Starch (amidin)	$C_{12}H_{10}O_{10}$
Dextrin	$C_{12}H_{10}O_{10}$
Inulin	$C_{24}H_{21}O_{21}$
Gum (arabin)	$C_{12}H_{11}O_{11}$
Bassorin (tragacanth)	$C_{12}H_{10}O_{10}$
Cellulin (cellulose)	$C_{36}H_{30}O_{30}$

Mannite	$C_{12}H_{14}O_{12}$
Dulcite (dulcose)	$C_{12}H_{14}O_{12}$
Pinite	$C_{12}H_{12}O_{10}$
Erythromannite	$C_{14}H_{16}O_{12}$
Quercite	$C_{12}H_{12}O_{10}$

Glycyrrhizin	$C_{48}H_{36}O_{18}$
Pectin	$C_{64}H_{40}O_{56}+8\,Aq$

Certain only of these substances are soluble in cold water, such as the sugars and the gums. Others, like starch, become dissolved in water by the aid of heat, or rather become diffused through the liquid, though the solution is of a very imperfect character; whilst a third variety, cellulin or ligneous fibre, is quite insoluble in water, whether hot or cold.

§ I. The Sugars.

(932) Several varieties of sugar are known to the chemist; but they may all be referred to three principal forms, viz., cane sugar or sucrose, grape sugar or glucose, and milk sugar or lactose. The most important of these is the common sugar, furnished by the sugar cane, hence termed *cane sugar*, related to which are some others of small importance, viz., trehalose, melezitose, and melitose. The second variety constitutes the hard granular sweet masses common in old dried fruits, such as raisins, figs, &c., when it is known as *grape* or *starch sugar*, the latter name being derived from a method of preparing it artificially by boiling starch with a dilute acid. The third variety is that to which milk owes its sweetness: it has never been met with excepting in the milk of animals, and hence it is termed *milk sugar*.

These different varieties of sugar agree in possessing a powerfully sweet taste. Each, when pure, has always a definite degree of sweetness, but there are great differences in the relative sweetness of the different varieties. A pound of cane sugar, for example, will produce a greater sweetening effect than a pound of fruit or inverted sugar; and at least two pounds and a half of starch sugar are required to produce a sweetening effect equal to that of one pound of the cane sugar; while a given weight of the sugar from milk possesses less sweetening power than an equal quantity of starch sugar.

These varieties of sugar differ greatly in external appearance as well as in chemical characters; and they also differ in chemical composition. If quantities of the different kinds of sugar which contain equal amounts of carbon be compared together, it will be found that they differ in the proportion in which the elements of water are present. Comparing together quantities of sugar which contain 12 atoms of carbon, the proportion of water in each variety will be as follows:—

Name of Sugar.	Formulæ.	Carbon.	Water.
Cane Sugar . .	$C_{12}H_{11}O_{11}$	72	99
Inverted Sugar .	$C_{12}H_{12}O_{12}$	72	108
Starch Sugar . .	$C_{12}H_{12}O_{12}+2\,Aq$	72	126
Milk Sugar . .	$C_{24}H_{24}O_{24}$	72	108

There are few plants from which sugar is absent, and to which, at some period of their growth it does not form an important article of nutriment.

(933) 1. CANE SUGAR or *Sucrose* ($C_{12}H_{11}O_{11}=171$).—This variety of sugar is chiefly obtained from the sugar cane; but the sugar maple and the beetroot furnish a considerable quantity for the market; it is also contained in carrots and turnips, as well as in the pumpkin, the chestnut, the young shoots of the maize, the ripe sorgho grass, and in a large number of tropical fruits.

Properties.—Cane sugar has a sp. gr. of 1·6. It is soluble in about one third of its weight of cold water, producing the thick, viscid liquid known as syrup. It is also somewhat soluble in alcohol, especially when heated with this liquid. By the spontaneous evaporation of its aqueous solution, it is deposited in large four-sided oblique rhomboidal prisms, which are often hemihedral, and are terminated by dihedral summits: these crystals constitute sugar candy, which is colourless or brown according as the syrup employed is more or less free from colour. Ordinary loaf sugar consists of a congeries of minute transparent crystals, and the a large proportion of formic and ids enter into combination

of *Sugar.*—Concentrated troys cane sugar. If equal triol be mixed, much heat is nts carbonic and formic acids, due containing ulmic acid is left. produced by some of the metallic posed to take advantage of this for mall quantities of sugar when in solution are to be dipped into a solution of ual quantity of water, and dried at 212°: ontaining sugar be placed on a slip so ted, a brown or black stain will be formed: obtained with glucose. Dry chlorine like- a temperature of 212°, and produces a similar hich is only partially soluble in water. Nitric 1·25, converts sugar into saccharic acid (944), carbonic acid; but if the nitric acid be more oxalic acid is formed.

undergoes an important change under the influence of beer, which causes it to experience the alcoholic : it first assimilates the elements of water, and is then into carbonic acid and alcohol (965). In contact with casein and chalk, lactic fermentation is induced in sugar, et being lactic acid (969); under other circumstances, yet thoroughly investigated, sugar undergoes the viscous ntation, and becomes changed into a mucilaginous substance, metimes into mannite (945).

36) *Action of Heat on Sugar.*—At a temperature of about F., sucrose undergoes fusion, and on cooling, forms the trans- amber-coloured solid, sold by the confectioners as *barley* If long kept in this form it loses its transparency, and lly becomes crystallized. This change may be retarded, but together prevented, by adding a small proportion of vinegar melted sugar. This alteration in structure is strictly us to that in virtue of which the tough, transparent variety hur resumes its crystalline state. It has been observed both these cases an evolution of heat occurs during the of the bodies from the vitreous to the crystalline condi- Another interesting point of resemblance between these nomena is presented in the remarkable difference between

manner, dissolved by syrup to a large extent; the compound ($CaO,C_{12}H_{11}O_{11}$; Péligot) is that which is produced in cold moderately dilute solutions; it has a bitterish taste, and is very soluble in cold water. Its solution, however, if tolerably concentrated, becomes opaque when heated, and presents an appearance of coagulation, resembling that of white of egg; and a deposit occurs on boiling, which may even be washed with boiling water, though it is readily redissolved by the mother liquor on cooling. If this precipitate be filtered from the boiling solution it is found to contain $3CaO, C_{12}H_{11}O_{11}$, and is nearly insoluble both in cold and hot water, though freely soluble in cold syrup. Baryta also forms a soluble compound with sugar ($BaO,C_{12}H_{11}O_{11}$).* The compounds produced with other bases are sparingly soluble in water, but are readily taken up by alkaline liquids. This fact explains an observation that the presence of sugar prevents the precipitation by alkalies, of many metallic oxides from their salts,—the oxides of copper and of iron being amongst the number thus retained in solution. Many metallic oxides experience reduction, either partial or complete, when boiled with sugar; if the chromates, for instance, be mingled with a little free acid, and heated with a solution of sugar, the chromic acid is reduced to the sesquioxide of chromium, which is dissolved by the excess of acid, whilst the liquid becomes green. Salts of the red oxide of mercury are converted into those of the suboxide, and salts of gold give a precipitate of the reduced metal in fine powder. This reducing action is also possessed, though to a less extent, by other compounds analogous to sugar.

If sugar be mixed with 8 times its weight of quick-lime, and distilled in an earthenware retort, it is decomposed, and amongst the products of the distillation are a mixture of acetone ($C_6H_6O_2$), and *metacetone* ($(C_6H_5O)_2$). The latter is an oily liquid, which does not mix with water, but is soluble in alcohol and in ether; by washing the distilled liquid with water, the acetone may, therefore, be removed, whilst the metacetone is left. Metacetone boils at 183° F. (Fremy). When treated with a mixture of bichromate of potash and sulphuric acid it undergoes oxidation, and is converted into propionic acid ($HO,C_6H_5O_3$; 1113). If sugar be treated with three times its weight of hydrate of potash, instead of with quickme, propionic acid, mixed with a large proportion of formic and etic acids, is formed, and the three acids enter into combination ith the potash.

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* Dubrunfaut and Péligot have taken advantage of the insolubility of these compounds in boiling water, to separate crystallizable sugar from treacle. Péligot has obtained one fourth of its weight from common treacle, by dissolving the precipitated sucrate of lime in water, and separating the lime by means of a current of carbonic acid.

(935) *Other modes of decomposition of Sugar.*—Concentrated lphuric acid rapidly chars and destroys cane sugar. If equal olumes of strong syrup and oil of vitriol be mixed, much heat is volved, the mass froths up and emits carbonic and formic acids, hilst a black carbonaceous residue containing ulmic acid is left. similar blackening effect is produced by some of the metallic hlorides; Maumené has proposed to take advantage of this for he purpose of discovering small quantities of sugar when in soluion:—Strips of white merino are to be dipped into a solution of ichloride of tin in an equal quantity of water, and dried at 212°: a drop of any liquid containing sugar be placed on a slip so repared, and gently heated, a brown or black stain will be formed: similar result is also obtained with glucose. Dry chlorine likeise attacks sugar at a temperature of 212°, and produces a similar rown substance, which is only partially soluble in water. Nitric cid, of sp. gr. of 1·25, converts sugar into saccharic acid (944), ith evolution of carbonic acid; but if the nitric acid be more oncentrated, oxalic acid is formed.

Cane sugar undergoes an important change under the influence of the yeast of beer, which causes it to experience the alcoholic ermentation; it first assimilates the elements of water, and is then decomposed into carbonic acid and alcohol (965). In contact with putrefying casein and chalk, lactic fermentation is induced in sugar, the product being lactic acid (969); under other circumstances, not as yet thoroughly investigated, sugar undergoes the viscous fermentation, and becomes changed into a mucilaginous substance, and sometimes into mannite (945).

(936) *Action of Heat on Sugar.*—At a temperature of about 320° F., sucrose undergoes fusion, and on cooling, forms the transparent amber-coloured solid, sold by the confectioners as *barley sugar.* If long kept in this form it loses its transparency, and gradually becomes crystallized. This change may be retarded, but not altogether prevented, by adding a small proportion of vinegar to the melted sugar. This alteration in structure is strictly analogous to that in virtue of which the tough, transparent variety of sulphur resumes its crystalline state. It has been observed that in both these cases an evolution of heat occurs during the passage of the bodies from the vitreous to the crystalline condition. Another interesting point of resemblance between these two phenomena is presented in the remarkable difference between

the melting points both of crystallized and vitreous sulphur, and of crystallized sugar and barley sugar. The latter becomes liquefied between 194° and 212°, while loaf sugar does not melt below 320°. According to Gélis, when sugar which has thus been melted is dissolved in water it furnishes a solution which when fermented with yeast yields only half the quantity of alcohol that ordinary sugar would have produced, a peculiar body to which he gives the name of *saccharide* ($C_{12}H_{10}O_{10}$) remaining in solution. It exerts a slight rotatory power to the right upon a beam of polarized light.

A solution of cane sugar exerts a right-handed rotation upon a ray of polarized light (120); but sugar which has long been kept in a melted state, when redissolved in water has lost its power of crystallizing, and no longer exerts any rotatory action on the polarized ray. Soubeiran also observed that when a solution of sugar is long exposed to an elevated temperature, even when air is excluded, it undergoes a molecular change; the liquid becomes brown, and gradually acquires a left-handed rotatory action upon the ray. The simple boiling of cane sugar with water, if long continued, causes the sucrose to combine gradually with the elements of water, and it thus becomes converted into starch sugar. This change is effected much more rapidly in the presence of chloride of ammonium, or of any of the chlorides of the metals of the earths, such as chloride of calcium.

If the application of heat to the melted sugar be continued, and it be gradually raised to 400° or 420°, each molecule ($C_{12}H_{11}O_{11}$) of sugar loses 2 Aq, and a brown deliquescent and nearly tasteless mass remains, which is known as *caramel* ($C_{12}H_9O_9$). This body is often used by cooks and confectioners as a colouring matter. Caramel is soluble in water, and is precipitated from its solution as a brown powder, by adding a large excess of alcohol. It is not susceptible of fermentation with yeast. Caramel forms an insoluble compound with baryta; and if its solution be mixed with one of the basic acetate of lead, a precipitate is formed. If sugar or caramel be heated beyond 420°, inflammable gases escape, and the compound is completely decomposed, leaving a porous brilliant mass of charcoal.

(937) 2. Fruit Sugar ($C_{12}H_{12}O_{12}$).—This was formerly supposed to be a distinct variety of sugar; but the researches of Buignet have shown that many ripe acidulous fruits contain cane sugar mixed with a variable proportion of *inverted* sugar. There is no variety to which the term of fruit sugar is exclusively applicable.

nverted sugar has received this appellation from its inverted n upon polarized light, which distinguishes it from sucrose; pears to be procurable only from sucrose, by the action either ids or of a peculiar albuminous ferment, present in the juice ny ripening fruits.

nverted sugar is not crystallizable; it is soluble in alcohol of r cent. If a solution of 5 parts of this sugar in 50 of water ixed intimately with 3 parts of slaked lime, the solution, is at first very liquid, becomes pasty: on straining it through and expressing the fluid portion, the sugar is separated into qual portions of different properties. One of these varieties ns in solution, and exerts a right-handed rotation upon a of polarized light, as may be ascertained by removing the y means of oxalic acid; whilst the other, which remains ed with the lime, exerts a left-handed rotation, and may be manner separated from the lime by suspending the com- in water and decomposing it by means of oxalic acid. hese forms of sugar are regarded as modifications of glucose. e sugar of fruits under the influence of diluted acids becomes ed with an additional quantity of water, and by continued of this acid liquid the sugar gradually passes into the form ose. When its solution, after the neutralization of the carbonate of baryta, is evaporated, the grape sugar is ob- in the form of crystals. This passage of the sugar in fruits ape sugar sometimes takes place spontaneously, as is seen gradual crystallization of the sugar in dried fruits. The ontained in honey by long keeping also undergoes a spon- change into a mass composed chiefly of crystalline grains h sugar.

8) 3. GRAPE OR STARCH SUGAR; *Glucose*,* ($C_{12}H_{12}O_{12}+$ 180+18).—*Preparation.*—Starch sugar is prepared upon erable scale by allowing a mixture of starch, with a sufficient y of water to render it liquid, to flow gradually at a tem- e of about 130°, into a vat containing water acidulated with nt. of sulphuric acid; this liquor is kept constantly at the point, by which means the starch is at once altered so as produce a mucilage. The liquid, after all the starch has

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der the name of *glucose* several distinct modifications of sugar have prised, such as linen sugar, uncrystallizable diabetic sugar, and gar, as well as sugar from malt, modified cane sugar, and the modi- f milk sugar produced by acids; but these bodies, though closely ng each other, present differences in their molecular structure, as may d by the differences in the effects produced by them on polarized light.

been added, is maintained in a state of ebullition for about half an hour, at the end of which time the starch is usually completely converted into sugar. The proportion of starch used amounts to one half of the weight of the water employed. The liquid is drawn off, and the acid is neutralized by adding chalk in small quantities at a time, until it ceases to occasion any effervescence; the precipitate is allowed to subside, and the clear solution is concentrated by evaporation until it acquires a density of 1·28. It is drawn off from the deposited sulphate of lime, after which it is set aside for some days to crystallize. The molasses is allowed to drain off, and the sugar is dried at a gentle heat in a current of air.

The formula usually assigned to starch is $C_{12}H_{10}O_{10}$, and since that of starch sugar may be represented as $(C_{12}H_{14}O_{14})$, the conversion of starch into sugar may be regarded in the light of a mere combination of starch with the elements of water.

Starch is also converted partially into a fermentable sugar resembling glucose, by the action of diastase (947).

A similar conversion of ligneous fibre into this form of sugar may be effected under the influence of acids, but in this case the acid is employed in a more concentrated form; 2 parts of clean linen or calico cut into shreds, are added gradually to 3 parts of oil of vitriol, and allowed to stand for 24 hours. The mixture is afterwards diluted largely with water, and boiled for a few hours. The acid may then be neutralized by the addition of chalk, or, what is better, of carbonate of baryta, and the sugar can afterwards be separated from the insoluble sulphate of lime, or sulphate of baryta.

True glucose is also produced from cane sugar by prolonged boiling with diluted acids, as well as from trehalose and melezitose when similarly treated. It is also furnished by amygdalin, salicin, phloridzin, and other glucosides (1302) when decomposed by acids. Chitin, or the horny covering of beetles and other insects, also yields it when treated with dilute acids.

Glucose appears to be the form of sugar which is occasionally met with as a morbid constituent of the urine in cases of diabetes. It has been shown by Bernard to be rapidly produced from one of the normal constituents of the liver, and the same physiologist has remarked, that by irritating with a needle the fourth ventricle of the brain in a dog or a rabbit, sugar is developed in the blood and in the urine, after a few minutes.

Properties.—Grape sugar is distinguished from cane sugar by several characters; it crystallizes with difficulty in warty concretions, composed of hard transparent cubes. It is considerably less soluble in water than cane sugar, though it is more readily taken up by alcohol, and crystallizes from a hot solution of alcohol containing not more than 5 per cent. of water, in anhydrous prisms ($C_{12}H_{12}O_{12}$). It requires nearly 2½ parts of glucose to produce the same sweetening effect as is produced by 1 part of cane sugar. The action of sulphuric acid upon grape sugar is quite different from its effect upon cane sugar, since, instead of decomposing it as occurs with sucrose, it forms with glucose a definite compound acid, which has been termed *sulphosaccharic acid*, and which, according to Péligot, yields a soluble salt with lime and with baryta.

Glucose forms with common salt a compound that crystallizes with facility [$NaCl, 2\,(C_{12}H_{12}O_{12}) + 2\ Aq$], thus furnishing another distinctive character of this variety of saccharine matter. This compound when heated to 212° gives off 2 Aq, and if the temperature of the residue be raised to 320° it loses an additional atom of water. When grape sugar is heated, it begins to soften at about 140°, and at 212° it melts and loses 2 Aq; at 284°, three additional atoms of water are expelled, and the residue consists of caramel.

Grape sugar forms definite but unstable combinations with the alkaline bases. These compounds, even at ordinary temperatures, gradually undergo change; their solution, which is at first strongly alkaline, becomes neutral, owing to the formation of a powerful, colourless, but uncrystallizable acid, *glucic acid* ($3\ HO,C_{24}H_{15}O_{15}$; Péligot), which remains in combination with the base. Glucic acid, when boiled with water, absorbs oxygen and becomes brown; a new acid ($2\ HO,C_{18}H_{9}O_{8}$), which Mulder terms *apoglucic acid*, is formed: it is not crystallizable. If an alkaline solution of grape sugar be heated, the sugar is rapidly destroyed, and a different body of dark brown colour, also possessed of acid characters, is produced; this substance is not crystallizable; it has been termed *melassic acid*. This body has a powerful affinity for oxygen, and when boiled with an alkaline solution, to which a salt of black oxide of copper has been added, speedily reduces the black oxide of this metal to the condition of the red oxide.

Estimation of Sugar.—Upon the foregoing facts Barreswil has founded a simple method of estimating the amount of sugar which any mixture may contain. For this purpose he prepares an alkaline solution of tartrate of copper and potash, of known strength. A given volume of this solution is placed in a porcelain capsule, and heated to near its boiling point; the solution of sugar to be tested is then added by degrees from a burette, until the addition of the syrup ceases to produce any further precipitate. The proportion of sugar which is present in the liquid will be inversely as the volume of the saccharine solution consumed. Cane sugar, however, does not reduce the alkaline solution of tartrate of copper, consequently no indication of the presence of cane sugar is afforded by this reagent. Nevertheless, a quantitative determination even of this variety of sugar may be effected by means of this method, provided that a given volume of the saccharine liquid, acidulated slightly with sulphuric acid, be diluted with water, and boiled for a short time; the cane sugar is thus converted into *inverted* sugar, and on diluting this liquid with water till it occupies a definite volume, the proportion of altered sugar which it contains may be ascertained. Supposing both kinds of sugar to be present, a preliminary experiment is made before boiling with acid, in order to estimate the amount of inverted or of grape sugar, and by deducting this from the quantity found after acidulating the liquid and boiling, the proportion of cane sugar is ascertained. Fehling recommends for the preparation of the standard copper solution, the following proportions as reduced to English weights:—1 ounce of crystallized sulphate of copper, 3 ounces of cream of tartar, 1¼ ounce of pure carbonate of potash, 14 or 16 ounces of a solution of caustic soda (sp. gr. 1·12), and water, which is added until the solution measures 15160 water grains. Two hundred measured grains of this solution contain a quantity of copper, which would be reduced by 1 grain of sugar ($C_{12}H_{12}O_{12}$); each atom of sugar reducing 10 atoms of the black oxide of copper to the state of suboxide. This test is often conveniently resorted to as a preliminary trial for sugar in urine: little or no action occurs when a solution of grape or diabetic sugar is mixed with an alkaline solution of copper in the cold; but on the application of a gentle heat the yellow hydrated suboxide of copper is thrown down, and on raising the temperature to the boiling point the red anhydrous suboxide is deposited. When a solution of any of the varieties of glucose is mixed with an ammoniacal solution of acetate of lead a precipitate is formed, containing ($3PbO,C_{12}H_{12}O_{12}$). Peroxide of lead converts glucose into a mixture of formiate and carbonate of lead, whilst water is eliminated.

(939) *Effects of the Varieties of Sugar on Polarized Light.*—Both sucrose, or cane sugar, and glucose produce rotation upon a ray of polarized light. The plane of polarization is rotated from left to right, by sucrose rather less powerfully than by glucose. It is remarkable that the uncrystallizable sugar of fruits produces an opposite rotation, viz., from right to left. Since the degree of

rotation is proportionate in columns of equal length to the quantity of sugar present, it has been proposed to employ this property in order to determine the quantity of sugar present in syrups. The following according to Berthelot are the rotatory powers of the different varieties of sugar, if equal weights of each are dissolved in an equal bulk of water: the quantities of each sugar are calculated for the formulæ annexed:—

				Temp.
Cane sugar	$(C_{12}H_{11}O_{11})$	right	73°·8	
Trehalose	$(C_{12}H_{11}O_{11})$	,,	220°	
Melezitose	$(C_{12}H_{11}O_{11})$	,,	94°·1	
Mycose	$(C_{12}H_{11}O_{11})$	,,	193°	
Melitose	$(C_{12}H_{12}O_{12})$	,,	102°	
Grape sugar	$(C_{12}H_{12}O_{12})$	,,	57°·4	
Malt sugar	$(C_{12}H_{12}O_{12})$	,,	172°	
Fruit sugar	$(C_{12}H_{12}O_{12})$	left	106°	56°
Eucalyn	$(C_{12}H_{12}O_{12})$	right	50°	
Sorbin	$(C_{12}H_{12}O_{12})$	left	46°·9	
Milk sugar	$(C_{12}H_{12}O_{12})$	right	56°·4	
Glucose of ditto	$(C_{12}H_{12}O_{12})$	,,	83°·3	
Inverted cane sugar	$(C_{12}H_{12}O_{12})$	left	28°	57°

In a paper contained in the *Ann. de Chimie*, III. xxvi. 175, Clerget gives a detailed account of the application of polarized light to the analysis of saccharine solutions by the aid of an instrument invented by Soleil. Bence Jones has applied the method to the determination of the quantity of sugar which remains in the unfermented state in wines. Diabetic urine may also be examined by the same process. According to Clerget, if the right-handed rotatory power of a given weight of cane sugar be taken as 100, that of an equal weight of diabetic sugar is 73, the rotation in this case also being right-handed. In connexion with the optical examination of syrups, the following facts are important:—Starch sugar presents three modifications when examined by its effect upon polarized light. A solution of crystallized starch sugar, when freshly made, possesses a rotatory power double of that which it retains after having been kept in solution for some hours; and the rotatory power of a solution of sugar from malt when freshly made, is three times as great as that of the same solution after long keeping. These different varieties may all be immediately reduced to the one possessed of the minimum rotatory power, by simply heating the solution to 180° or upwards, and then allowing it to cool. If the rotatory power of starch sugar, of minimum effect, be taken as 1, that of a fresh solution of crystallized starch sugar will be 2, that of sugar of malt 3, and that of an equivalent quantity of dextrin (950) will be equal to 4. Sugar of milk, and the modified fermentable sugar obtained from it by the action of acids, resemble starch sugar in the circumstance that when first dissolved in water their solutions exert a greater rotatory power than after they have been in solution for a few hours. After the lapse of a certain interval of time the rotatory effect becomes stationary, and is represented by the numbers given in the table.

Starch sugar after it has been thus reduced to its minimum power of rotation, undergoes no change when heated for a short time with an acid; but the rotatory power from left to right, possessed by a solution of cane sugar, is reversed by mixing the liquid with one tenth of its bulk of a pure concentrated solution of hydrochloric acid, and heating it by means of a water bath for ten minutes to the temperature of 154°: the crystalline sugar is thus converted into an uncrystallizable form, distinguished as *inverted* sugar (937). It has been remarked, that the addition of a solution of potash or of soda to a solution of sugar, reduces the rotatory action of the liquid upon the polarized ray, but on neutralizing the alkali the original effect is restored. An excess of acid exerts no sensible effect upon the rotatory power of the liquid. Mitscherlich has shown that elevation of temperature produces a very singular effect upon the rotatory power. In the case of cane sugar, the rotatory power diminishes slowly as the temperature rises. If the rotatory power at 32° be=1, it will at 212° be less by 0·0232 (or=0·9768 Dubrunfaut); and in the case of cane sugar altered by acids the effect is so considerable, that according to Buignet it amounts to about 0·205° for each rise of 1° F.: indeed, not only is its rotatory power to the left greatly reduced, becoming at 126° only one half of that which it had at 57°, but at 187° it becomes null, and beyond this it is actually reversed, and becomes right handed.

(940) *Manufacture of Sugar.*—The chief source of sugar in the state in which it is offered for sale is the sugar-cane, of which there are three or four varieties. This plant is a solid, jointed reed, which grows to a height varying from 6 to 15 feet. The sugar-cane flourishes best between the tropics, and requires a strong deep soil. It is found most advantageous to cut the canes before they are allowed to flower, the produce of sugar being much reduced after inflorescence. The canes are cut as close to the soil as possible, since the juice contained in the lowest joints is the sweetest. The ripe canes immediately after cutting are stripped of their leaves, and subjected to strong pressure by passing them between grooved iron cylinders. In that hot climate the juice, if left to itself even for half an hour, begins to ferment: it is, therefore, immediately mingled with from $\frac{1}{3000}$th to $\frac{1}{800}$th of its

it of lime, and heated to 140° in large flat-bottomed copper
or clarifiers, which hold from 300 to 400 gallons each. At
temperature the albuminous portions of the juice become
ilated and rise to the surface in the form of scum, whilst the
cid is neutralized by the lime. After allowing it to cool for
ur, the clear liquid is drawn off for concentration by boiling.
uel used for this purpose generally consists of the crushed
the ashes of which, in well-managed plantations, are always
ed to the soil, and furnish manure for future crops. When
rup has acquired sufficient consistence, it is run into shallow
n coolers, and immediately stirred briskly for a few minutes;
hen left to stand for an hour, when a crust-like thin ice
s formed over the top; this is broken up, after which the
s left at rest for twenty-four hours; the semi-solid mass is
ansferred to the curing-house, and is put into the *potting*
which are vessels furnished with perforated bottoms to allow
lasses or treacle to drain off. Into each perforation a reed,
stem of a plantain-leaf, is placed, extending to the top of
t, with the view of facilitating the drainage, which requires
to 5 weeks for its completion. The crystals are finally
f in the sun, and form the raw sugar of commerce. On
age, one gallon of juice furnishes one pound of sugar.
aste is, however, incurred in the extraction of the saccha-
tter, for according to Dumas 100 parts of fresh cane should
of juice, and of this 18 or 20 parts are pure sugar. No
llizable sugar is contained in the fresh juice of sound
ough it occurs in decayed ones. Much of the waste arises
conversion of the crystallizable sugar into treacle or un-
able syrup, by the high temperature and frequent boilings
it is subjected. Great improvements have recently been
in the apparatus for boiling down syrups, by means of
beautiful crystallized product may with care be obtained
juice at the first crystallization.

le Sugar.—The American Indians manufacture a consider-
ntity of sugar from a species of maple (*Acer saccharinum*).
to obtain the juice, they make perforations which pene-
ough the bark from a quarter to half an inch into the
Each tree usually has two borings; these perforations are
made upon the side of the tree facing the south, at a
from 16 to 20 inches from the surface of the soil. Reeds
d in each aperture, to convey the juice into suitable
The best season of the year is during the months of
pril, and May, while *the sap is rising,*—from the 22nd of

March to the middle of April being the period preferred. S times a second running is taken in the autumn from the tree, but it is more injurious to the tree than the spring tap in autumn the juice does not run for more than four or five day it is twice as strong as that which is drawn in spring. A goo gives daily six gallons from each incision, and in an old tree or bush' these six gallons yield one pound of sugar. In a 'new b twelve gallons are required for each pound of sugar: the ave quantity of sugar from each tree is about three pounds. If perly treated, the same tree may be tapped for 20 or 30 yea succession. The higher the perforations the sweeter is juice. Every twenty-four hours the liquid that has colle is concentrated, and the raw crystallized sugar is sold in bl without further refining.

Beet-root sugar is extracted by pressing out the juice from ripe roots of the white beet, which are usually gathered in Octo The expressed juice contains about 10 per cent. of sugar, whic the fresh juice is entirely of the crystallizable kind; but i seldom possible to extract in the crystallizable form more than the quantity which the root contains.

The expressed juice is first mingled with a small quantity lime, and then boiled; a large portion of the albumen and azot matters are thus coagulated, and rise to the top in the form a scum, which is carefully removed. The juice is next filt through a column of animal charcoal; it is concentrated in vacuum pan and is then filtered a second time through charc it is again evaporated still further, and filtered through coarse cl bags to remove any suspended particles; after which it is bo down to the crystallizing point; the syrup at this stage havin sp. gr. of about 1·39.

The crystals of beet-root sugar are longer and flatter t those furnished by sugar from the cane, but they cannot other be distinguished from the latter.

The manufacture of sugar from this root was called into ex ence by the wars of Napoleon, during which the ordinary sup of the article was cut off from the French. In France, where principal manufactories of this sugar exist, a good deal of molasses, which is inferior to that of the cane, is fermented, furnishes a considerable quantity of spirit of wine, amountin weight to nearly one-third of the treacle employed; this spiri purified by distillation: the residuum is evaporated to dryness, then incinerated for the sake of the alkaline salts which it yie these salts consist principally of carbonates of soda and potash, a small proportion of sulphate of potash and of chloride of potassium. Beet-roots contain a large proportion of soluble saline matters, which are by this means economized. The crushed pulp is either employed while fresh as food for cattle, or used as manure for the land.

(941) *Refining of Sugar.*—The process of refining sugar, whether from the cane or the beet-root, is alike for each. Two or three parts of sugar are dissolved in 1 part of lime-water mixed with 3 or 4 per cent. of bone black, and the whole is heated in large cisterns by allowing steam to blow up into them through pipes which open into the bottom of the vessel; from these cisterns the syrup is transferred to a filtering apparatus consisting of tubes of twilled cotton, where it is freed from mechanical impurities, and runs through as a reddish brown syrup. In many establishments this clarification is aided by adding to the syrup a certain quantity of the serum of bullock's blood. The albumen of the serum, on the application of heat, becomes coagulated and rises to the surface, carrying with it entangled in its meshes the greater part of the solid impurities, which are afterwards removed by skimming.

The reddish syrup which has run through the filters has next to be freed as much as possible from colouring matter, and for this purpose it is a second time filtered; but the filter on this occasion is of a different nature, and consists simply of a bed of animal charcoal, prepared by calcining bones in closed vessels, and subsequently grinding them into a coarse powder. The filters consist of extensive vats 12 or 14 feet deep, with perforated false bottoms; upon these a layer of ticking is placed, and above this charcoal to the depth of 12 feet; above this is another layer of ticking covered with a perforated metallic plate. The syrup is allowed to flow evenly over the surface, and by the time it has run through it is colourless (53).

Owing to the viscidity of the filtered liquid, a high temperature (230°) is necessary to make it boil under ordinary circumstances: and at this temperature the sugar quickly passes into the uncrystallizable modification, especially when exposed to the action of the atmosphere. By an ingenious application of the mode in which liquids may be boiled *in vacuo* at a temperature far below their ordinary boiling point (169), this difficulty has been in a great measure overcome; and the syrups are now universally boiled down in the *vacuum pan*. In this apparatus the pressure of the atmosphere is removed by means of a powerful air-pump, and a vacuum is maintained above the surface of the liquid in the evaporating vessel, which is a closed pan or boiler constructed of a spheroidal form, in order to enable it to resist the pressure of the external atmosphere. The lower half of the pan is double, for the purpose of admitting steam between the coatings; and a spiral steam pipe is also coiled within the boiler, with a view of increasing the extent of heating surface. By this arrangement a supply of steam can be admitted from a neighbouring boiler, the heat being sufficient ot cause the syrup to enter in rapid ebullition, whilst all danger of burning the syrup is completely avoided; since the boiling point does not rise above 150° or 160°. The evaporation is continued until a small quantity of the liquid when placed between the thumb and finger can be drawn out into a thread, which breaks near the thumb and curls back to the finger. When it reaches this point the syrup is emptied into a vessel heated by steam to about 170°; in this *heater* it is strongly agitated with wooden oars until it appears to be thick and granular. It is upon this agitation in the heater that the whiteness and fineness of the grain in refined sugar depend. Fresh portions of the evaporated liquor are two or three times added to the first, and thus the temperature is alternately raised and suffered to fall. From the heating vat it is transferred into inverted conical moulds, either of sheet iron or of unglazed earthenware; in the apex of each of these is an aperture, which is at first closed by means of a plug. The syrup is again well stirred in these moulds, to favour the escape of air-bubbles, which would otherwise give the mass a honeycombed appearance. After this operation it is left at rest for several hours, at the end of which time the plug is removed, and the uncrystallized syrup runs into vessels placed below for its reception. The sugar, however, is not yet white; for though the crystals consist of pure sugar, the loaves retain mechanically a large quantity of coloured syrup. In order to get rid of this, a quantity of fine colourless syrup is poured upon the base of each loaf, and this syrup, as it gradually percolates through the porous mass, displaces the impurities. The loaf is finally dried in a heated chamber, and finished for the market by turning it in a lathe.

In many refineries, after the finest quality of sugar has been obtained in the form of loaves in the manner already described, the syrup which drains from them is boiled down again in the vacuum pan, and is obtained in the form of what is termed *crushed sugar*, which is freed from the uncrystallized syrup with great rapidity by an ingenious application of the centrifugal force. The apparatus employed is similar in principle to that which has been long used for drying clothes in laundries. It consists of a cylindrical drum mounted upon a vertical axis, to which a very rapid rotatory movement can be given. The outer wall of this revolving drum is formed of a stout but close metallic network. This drum is enclosed in a second somewhat larger fixed cylindrical vessel, in which the liquid portion of the syrup is collected. In order to use the apparatus, a charge of concentrated syrup, which has been allowed to cool, and has thus become converted into a crystalline magma, is transferred to the inner drum of the centrifugal machine. The drum is now put into rapid rotatory motion, the uncrystallized syrup escapes through the pores of the metallic gauze, whilst the crystals are retained upon its inner surface. Between the withdrawal and the introduction of each charge the drum is cleansed by a jet of high-pressure steam, and thus the pores of the metallic network are kept clear.

(942) *Melitose* ($C_{24}H_{24}O_{24}+4\,HO$).—This is the name given by Berthelot (*Ann. de Chimie*, III. xlvi. 66) to a singular modification of sugar observed by Johnston to be contained in the manna of some species of the *Eucalyptus*. It is soluble in water, and somewhat soluble in alcohol. Its aqueous solution crystallizes by spontaneous evaporation in slender needles, which have a feebly sweet taste. When heated to 212° it loses 4 Aq, or 9·2 per cent. of water; if heated to 266° it loses about 1 atom more of water, melts, and emits an agreeable odour, whilst it assumes the aspect of barley-sugar. The aqueous solution of melitose produces right-handed rotation of a polarized ray more powerfully than one of cane sugar. Basic acetate of lead produces a precipitate in its solutions. It does not reduce the salts of copper when boiled with an alkaline solution of these compounds; but if boiled with sulphuric acid, the resulting liquid acquires the power of reducing the salts of copper, and its rotatory power is reduced by two-fifths, but it is not inverted like that of cane sugar. With nitric acid it yields, amongst other products, mucic acid. When mixed with yeast, melitose experiences the vinous fermentation, but it gives off one half only of the quantity of carbonic acid which an equal weight of glucose would have yielded. These peculiarities depend upon the fact that under the influence of acids and of yeast melitose becomes broken up into two portions, one of which is susceptible of fermentation like glucose, whilst the second portion remains unacted on in the liquid. To the latter body the name of *Eucalyn* has been given. It is a substance of syrupy consistence, and a feebly sweet taste; when dried *in vacuo* at the ordinary temperature, it consists of $C_{12}H_{12}O_{12}+2\,HO$, and at 212° it parts with 2 HO. It produces right-handed rotation upon a polarized ray. Eucalyn has the properties of sorbin (*see table, p. 96*) in every respect,

except that sorbin produces left-handed rotation and is crystallizable. When heated with alkalies it assumes a brown colour, and reduces the salts of copper; at a heat of 392° it becomes converted into a black insoluble mass. Melitose appears therefore to be formed by the union of two varieties of sugar, one of which is fermentable under the influence of yeast, while the other is not so.

(943) SUGAR OF MILK; *Lactin* or *Lactose* ($C_{24}H_{24}O_{24}$, or $C_{24}H_{19}O_{19} + 5\,HO$), *Sp. Gr.* 1·543.—This variety of sugar is an animal product, being obtained solely from the milk of the mammalia. It is produced by the herbivora in greatest abundance, but it is secreted also by the carnivora, although their diet is exclusively of an animal nature.

Preparation.—After the milk has been coagulated the curd is separated, and the whey is concentrated by evaporation until it reaches the crystallizing point; small pieces of wood are then introduced to act as nuclei upon which the crystals of lactose are deposited. It is thus procured in mammillated masses composed of groups of right four-sided prisms, terminated by four-sided pyramids. The crystals are white and semitransparent; they feel hard and gritty between the teeth, and require 5 or 6 parts of cold water for solution; the liquid thus formed is less sweet to the taste than that produced by an equal weight of starch sugar. Lactose is insoluble in alcohol and in ether. Its aqueous solution produces right-handed rotation of a ray of polarized light; the fresh solution has a higher rotatory power than it exhibits after standing for a few hours, or after heating it to 212°. If lactose be heated gradually to 284°, 2 Aq are expelled; but it is remarkable that if the temperature be suddenly raised to about 400°, the crystals melt, and then lose 5 Aq. When boiled with dilute acids it is very slowly converted into a fermentable sugar which exerts a right-handed rotatory action upon polarized light, and furnishes mucic acid when treated with nitric acid. When pure, milk-sugar is not susceptible of fermentation, but milk itself may be fermented. In this case, Berthelot was unable to find any evidence of the conversion of the lactose into glucose before it underwent fermentation. If the milk be allowed to ferment spontaneously in contact with chalk, a considerable quantity of lactate of lime is formed simultaneously with the alcohol. Lactose may be combined with oxide of lead, and forms with it two white insoluble compounds, $C_{24}H_{19}O_{19}, 5\,PbO$, and $C_{24}H_{19}O_{19}, 10\,PbO$. It also forms compounds with the alkalies and with the alkaline earths, and absorbs both ammoniacal and hydrochloric acid gases. An alkaline solution of lactose when boiled with the salts of copper reduces them, and precipitates the suboxide of the metal. It also reduces the salts of mercury and of silver when heated with their solutions.

(944) *Action of Nitric Acid on the Sugars.*—The action of nitric acid upon the different varieties of sugar is remarkable and characteristic. Sucrose and glucose, when treated with 3½ times their weight of nitric acid, of sp. gr. 1·27 (care being taken that the temperature be not allowed to rise beyond 160°), yield a peculiar acid, the *saccharic;* and the same substance may also be obtained from starch, gum, and lignin by similar treatment.

Saccharic Acid ($2\,HO, C_{12}H_8O_{14}$).—This acid forms a colourless, inodorous, deliquescent, gummy, uncrystallizable mass, which is freely soluble in alcohol, but sparingly so in ether. It yields two salts with potash, one of which is the normal salt; it contains 2 atoms of base to 1 of acid, and is very soluble: the other is a sparingly soluble acid saccharate which crystallizes in oblique rhombic needles. Saccharic acid is sufficiently powerful to dissolve iron and zinc with extrication of hydrogen. Its normal salt with baryta is amorphous and sparingly soluble. Saccharic acid has a tendency to form double salts, so that it appears to be dibasic.

If sucrose or glucose be acted upon by nitric acid, of a sp. gr. higher than 1·27, and the temperature be allowed to rise, a large quantity of oxalic acid is formed.

Mucic Acid ($2\,HO,C_{12}H_8O_{14}$).—Sugar of milk, when treated with excess of nitric acid, furnishes *mucic* acid, accompanied by saccharic acid, with which the mucic is isomeric; mucic acid may also be produced from gum and mannite by similar treatment. When sugar of milk is used, Liebig found the mother-liquor to contain tartaric acid; indeed it may be remarked that one molecule of mucic acid contains the elements of one molecule each of tartaric and acetic acids, for

$$\overbrace{C_{12}H_{10}O_{16}}^{\text{Mucic Acid.}} = \overbrace{C_8H_6O_{12}}^{\text{Tartaric Acid.}} + \overbrace{C_4H_4O_4}^{\text{Acetic Acid.}}$$

One part of gum or of sugar of milk, when boiled with 4 parts of nitric acid of sp. gr. 1·35 and 1 part of water, on cooling deposits mucic acid in minute, colourless, transparent, tabular crystals, which assume the appearance of a sparingly soluble white gritty powder, insoluble in alcohol. It is a dibasic acid, the salts of which are all insoluble in water with the exception of those of the alkalies: it forms two classes of salts, a neutral or normal, and an acid series. The normal mucate of potash consists of $2KO,C_{12}H_8O_{14}+Aq$; the bimucate of the same base, of

$KO,HO,C_{12}H_8O_{14}+Aq$. Mucic acid is soluble in concentrated sulphuric acid, with which it forms a crimson solution.

When mucic acid is heated, carbonic acid and water are expelled, and a new monobasic acid, the *pyromucic* ($HO,C_{10}H_3O_5$), is sublimed in delicate needles :—

$$2\ \overbrace{HO,C_{12}H_8O_{14}}^{\text{Mucic Acid.}}=\overbrace{HO,C_{10}H_3O_5}^{\text{Pyromucic Acid.}}+\overbrace{C_2O_4}^{\text{Carbonic Acid.}}+3\ H_2O_2.$$

Pyromucic is isomeric with pyromeconic acid, but it is distinguished from this body by the formation of a white insoluble precipitate when added to a solution of subacetate of lead.

If mucic acid be simply boiled in water for some time, it passes into an isomeric variety known as *paramucic acid*, which is much more soluble in water than mucic acid, and is also freely taken up by alcohol; when its aqueous solution is evaporated, paramucic acid is left in quadrangular tables.

The action of polybasic acids upon the sugars gives rise to a remarkable series of bodies which we shall describe hereafter (1073). The products thus obtained lead to the conclusion that glucose belongs to the class of polyatomic alcohols.

§ II. Other Soluble Substances allied to Sugar.

(945) Mannite ($C_{12}H_{14}O_{12}$ or $C_{12}H_{12}O_{10}+2\ HO$).—This substance constitutes the principal portion of the drug known as *manna*, the inspissated saccharine juice of the *Fraxinus ornus*, a tree which grows abundantly in Sicily and Calabria. Mannite is also contained in considerable quantity in celery, in onions, asparagus shoots, and in certain kinds of fungi. Stenhouse also found it largely in many species of seaweed; the *Laminaria saccharina*, when dried, containing as much as 12 or 13 per cent. of mannite. It is likewise a constituent of the juice which exudes from many varieties of apple and pear-trees; and it is always formed during the viscous fermentation of sugar to which the juice of the beet-root is particularly liable; so that it is a substance which, from its extensive distribution, acquires a certain degree of interest.

Mannite may be readily extracted from the manna of the *Fraxinus ornus* by digesting it in hot alcohol; as the solution cools, the mannite crystallizes in tufts of silky quadrangular prisms. It fuses at about 320° without losing weight, forming a colourless liquid, which, on cooling, solidifies into a mass of radiated crystals. Mannite may be heated in a sealed tube to 480° without experiencing decomposition; but when raised in the open air to a temperature not exceeding 400° it loses water, and a large portion is converted into a substance termed *mannitane* ($C_{12}H_{12}O_{10}$), which is a syrupy liquid closely analogous to glycerine; it has a sweetish taste. It is insoluble in ether, but freely soluble in water and in alcohol: if exposed to the air it deliquesces, and is slowly reconverted with assimilation of water into crystallized mannite:—

$$\overbrace{C_{12}H_{14}O_{12}}^{\text{Mannite.}} = \overbrace{C_{12}H_{12}O_{10}}^{\text{Mannitane.}} + H_2O_2.$$

Mannite is very soluble in water: it has an agreeable sweet taste, and is easily distinguished from cane sugar by the absence of any charring effect when it is treated with sulphuric acid; in fact, the acid combines with it and forms *sulphomannitic acid* ($HO,C_6H_5O_4,S_2O_6$). Mannite may also be distinguished from grape sugar with facility, since it does not become brown when heated with alkaline solutions. It combines with bases, and dissolves lime freely; this solution when boiled becomes turbid, but the precipitate is re-dissolved as the liquid cools. When a concentrated aqueous solution of mannite is mixed with one of ammoniacal acetate of lead, a precipitate ($C_{12}H_{10}O_8$, 4 PbO) is formed, which consists of mannite, in which 4 atoms of oxide of lead have displaced 4 HO. Solutions of mannite do not reduce the alkaline solution of tartrate of copper when boiled with it, but when heated with a solution of the nitrate of silver they precipitate the metal. They likewise reduce gold from a solution of its chloride.

Mannite is further characteristically distinguished from true sugar by its want of rotatory power upon a ray of polarized light. Nitric acid produces saccharic and oxalic acids when heated with mannite, but no mucic acid. Mannite when heated with the fatty acids furnishes compounds analogous to the fats (1072).

It is generally stated that mannite is insusceptible of the alcoholic fermentation, and it certainly does not ferment when its solution is mixed with yeast; but Berthelot has shown (*Ann. de Chimie*, III. l. 334) that if a solution of mannite be maintained for some weeks at a temperature of 100° F. in contact with chalk, and with a quantity of poor cheese, or of pancreatic tissue, or with some analogous azotised matter capable of acting as a ferment, it is partially fermentable, a quantity of alcohol, varying from [illegible] to 33 per cent. of the weight of the mannite used, being produced. Small quantities of lactic, butyric, and acetic acids are formed at the same time, and carbonic acid and hydrogen gases are liberated. The formation of alcohol from mannite may be represented by the equation,

$$\overbrace{C_{12}H_{14}O_{12}}^{\text{Mannite.}}=2\ \overbrace{C_4H_6O_2}^{\text{Alcohol.}}+2\ C_2O_4+H_2\ ;$$

two volumes of carbonic acid being liberated for each volume of hydrogen. The formation of lactic acid may be represented still more simply,

$$C_{12}H_{14}O_{12}=2\ \overbrace{(HO,C_6H_5O_5)}^{\text{Lactic Acid.}}+H_2.$$

The butyric and the acetic acids are secondary results of the decomposition of the lactic acid (1114) and of the oxidation of the alcohol (1078).

Berthelot states that he has succeeded in converting mannite into a variety of true sugar, susceptible of fermentation with yeast, by digesting it with several substances of organic origin. The organic body with which he succeeded almost uniformly in producing this effect was the tissue of the testicle, either of man, or of animals such as the cock, the horse, or the dog. In this experiment a solution of 1 part of mannite in 10 of water is digested at a temperature of 70° in an open flask upon the animal tissue, which should amount to about $\frac{1}{20}$th of the weight of the mannite (both estimated in the dry form). No putrefaction or mouldiness occurs if the operation be successful, and in the course of a few weeks the transformation is effected. The fragments of testicular tissue, if removed to a fresh solution of mannite, continue their sugar-producing action in this fresh solution. In a few cases as much as $\frac{1}{10}$ of the mannite employed was converted into sugar. This sugar resembles glucose, but has not yet been obtained in a crystalline form.

Glycyrrhizin ($C_{48}H_{36}O_{18}$, Gorup Besanez).—The sweet principle of the liquorice root is not a true sugar, for it is not susceptible of fermentation. It has a strong tendency to combine with bases, and it forms soluble compounds with the alkalies and alkaline earths. It is usually obtained by adding an acid to a concentrated decoction of liquorice root, washing the precipitate with cold water, and dissolving it in alcohol; on evaporating this solution, the glycyrrhizin is left in the form of a brilliant, transparent, brownish mass, which is sparingly soluble in cold water, especially if acidulated. It is more soluble in hot water, but its proper solvent is alcohol. The solution has a sweet taste, leaving a disagreeable bitterness upon the palate. If boiled for some hours with hydrochloric acid glycyrrhizin splits into a brownish resin and glucose.

e following table contains a summary of the leading cha- of the principal varieties of sugar, including those of a few ine substances of less importance—viz., *trehalose*, *melezitose*, *dulcite*, *quercite*, and *pinite*, which it will be unnecessary to e more minutely.

Sugars and some allied Bodies.

IT AND F SUGAR.	PRINCIPAL PROPERTIES.
se, or Sugar, $_{11}O_{11}$; gar cane.	Crystallizes in four or six-sided rhomboidal prisms—is very soluble in water, less so in dilute alcohol—sp. gr. 1·6—fuses at about 320° F.—is not precipitated by subacetate of lead, but is so by an ammoniacal solution of acetate of lead—does not reduce an alkaline solution of tartrate of copper on boiling—produces *right*-handed rotation = 73°·8,—undergoes alcoholic fermentation with yeast—combines with alkalies—yields glucose when boiled with dilute acids—with nitric acid yields saccharic and oxalic acids.
rted Sugar, $_{11}O_{11}$; ny recent its.	Is not crystallizable—is soluble in dilute alcohol—is not precipitated by subacetate of lead—reduces an alkaline solution of tartrate of copper by boiling—produces *left*-handed rotation = 26° at 59° F.—undergoes alcoholic fermentation with yeast—turns brown when treated with alkalies—is partially converted into grape sugar by boiling with dilute acids.
se, or Sugar, $_{12}$+2 HO; d fruits; starch by acids.	Crystallizes in cubes or square tables—is less soluble in water than cane sugar, but more soluble in alcohol—yields a precipitate with ammoniacal acetate of lead—reduces tartrate of potash and copper, and the salts of mercury, silver, and gold when boiled with them—ferments readily with yeast—produces *right*-handed rotation = 57°·4—becomes brown when treated with alkalies—with nitric acid yields saccharic and oxalic acids.
se, or f Milk, 5 HO; whey of lk.	Crystallizes in four-sided prisms—is less soluble in water than grape sugar—is nearly insoluble in alcohol and ether—is precipitated from its solutions by ammoniacal acetate of lead—reduces the salts of copper, silver, and mercury when its alkaline solution is boiled with them—produces *right*-handed rotation = 56°·4—is not directly susceptible of alcoholic fermentation—is converted into glucose by boiling with dilute acids—yields mucic and oxalic acids with nitric acid.
alose, $_{11}$+2 Aq; lelot.) Manna, of insect s nidifi- us.	Crystallizes in brilliant rectangular octohedra—produces *right*-handed rotation = 220°—if heated quickly it fuses at 212°, and loses its water of crystallization—is very soluble in water, and in hot alcohol—sparingly soluble in cold alcohol and ether—is precipitated by ammoniacal acetate of lead—does not reduce the tartrate of copper and potash by heat—ferments slowly and imperfectly with yeast—yields glucose when heated with dilute acids—does not give mucic with nitric acid.
ose, O_{11} 2 Aq; rlich) of rye	Crystallizes in rhombic prisms—melts at 212°, and at 266° loses 2 Aq, and becomes solid—may be heated without decomposition to 410°, when it melts again—is easily soluble in water, very slightly so in alcohol—does not reduce an alkaline solution of tartrate of copper—exerts *right*-handed rotation = 193°—with nitric acid yields saccharic and oxalic acids.

VARIETY AND ORIGIN OF SUGAR.	PRINCIPAL PROPERTIES.
Melezitose, $C_{12}H_{11}O_{11}+x\,Aq$; (Berthelot) from larch manna.	Crystallizes in short, hard, efflorescent rhomboidal is very soluble in water—sparingly soluble in alcohol, or cold—insoluble in ether—has a sweetness about that —fuses at 280°—is precipitated by ammoniacal acetate does not reduce the alkaline tartrate of copper—produ handed rotation = 94°·1—ferments with difficulty—yiel when heated with dilute acids—gives no mucic acid acid.
Melitose, $C_{24}H_{24}O_{24}+4\,HO$; (Berthelot) from the *Eucalyptus*.	Crystallizes in slender prisms—is freely soluble i slightly soluble in alcohol—is feebly sweet—melts water at 260°—yields a precipitate with ammoniacal lead—does not reduce an alkaline solution of tartrate of exerts *right*-handed rotation = 102°—undergoes alcohol tation with yeast, at the same time half the sugar is in an unfermentable form as Eucalyn—furnishes mucic nitric acid—is little affected by alkalies.
Eucalyn, $C_{12}H_{12}O_{12}+2\,HO$; (Berthelot) from fermentation of melitose.	Is not crystallizable—precipitates ammoniacal acetat and reduces the alkaline tartrate of copper when boiled produces *right*-handed rotation = about 50°—is not sus alcoholic fermentation with yeast—becomes brown wh with alkalies—is not altered by boiling with dilute acid
Sorbin, $C_{12}H_{12}O_{12}$; (Pelouze) from berries of service tree *Sorbus aucuparia*.	Crystallizes in octohedra with a rectangular base—is water—nearly insoluble in alcohol—sp. gr. 1·65—is fu out loss of weight—gives a white precipitate with a acetate of lead—reduces the alkaline solution of tartrat on heating it with it—occasions *left*-handed rotation = not fermentable with yeast—becomes brown when tr alkalies—yields a red solution with oil of vitriol—is con oxalic acid by nitric acid.
Inosin, $C_{12}H_{12}O_{12}+4\,HO$; (Scherer) from muscular tissue.	Crystallizes in radiated tufts—is soluble in water in absolute alcohol and ether—loses water by heat, a 410°—has no rotatory power on polarized light—does the alkaline tartrate of copper when boiled with it—is tible of alcoholic fermentation, but with cheese and lactic and butyric acids—is not altered by boiling with or alkalies—forms a precipitate with ammoniacal aceta
Mannite, $C_{12}H_{14}O_{12}$; from the juice of *Fraxinus Ornus*.	Crystallizes in silky anhydrous four-sided prisms in water and alcohol—fuses at 320°—gives a preci ammoniacal acetate of lead—reduces the salts of silver heat—does not reduce the alkaline tartrate of copper with it—exerts no rotatory power of polarized light—is fermentable—with nitric acid yields saccharic and oxal soluble without coloration in oil of vitriol, and in alk tions.
Erythro-mannite, $C_{14}H_{16}O_{12}$; (Gerhardt,) from Roccella and other lichens.	Crystallizes in broad voluminous crystals of the system—is soluble in water and in alcohol—fuses at no precipitate with ammoniacal acetate of lead—does the alkaline tartrate of copper—yields no mucic acid acid—is not fermentable.
Dulcite, $C_{12}H_{14}O_{12}$; (Laurent) origin unknown.	Crystallizes in brilliant prisms—is soluble in water an —fuses at 356° F.—gives no precipitate with acetate acetate of lead—does not reduce nitrate of silver or gold—produces no rotation on polarized light—is not of fermentaion with yeast—is not affected by dilute converted into mucic acid by nitric acid.

IETY AND ES OF SUGAR.	PRINCIPAL PROPERTIES.
Quercite, ${}_{12}H_{11}O_{10}$; m acorns.	Crystallizes in transparent prisms—is soluble in water and dilute alcohol—is fusible at 420°—does not reduce the alkaline tartrate of copper—is not fermentable by yeast—is soluble without change of colour in oil of vitriol and in the alkalies—yields oxalic acid with nitric acid.
Pinite, ${}H_{12}O_{10}$; rthelot,) m *Pinus* *bertiana*.	Crystallizes slowly in hard hemispherical radiated masses—has a very sweet taste—is very soluble in water—sparingly so in alcohol—gives a precipitate with ammoniacal acetate of lead—does not reduce the alkaline tartrate of copper—sp. gr. 1·52—produces *right*-handed rotation—is not fermentable—fuses below 480°—does not yield mucic with nitric acid.

§ III. Varieties of Starch and Gum.

6) Starch ($C_{12}H_{10}O_{10}$).—The term *starch*, or *amylaceous* , or *fecula*, is applied to an organized substance which in rounded or oval grains in the cellular tissue of certain f plants. It is met with in great abundance in all dicotyus seeds, particularly in those of leguminous plants, such as nd beans. The monocotyledonous seeds of the *Cerealia* or ibe contain it still more largely: it is also abundant in the of the potato, in the roots of the tapioca and arrow-root, a variety of other plants. On examining the grains of with a magnifying power of 300 or 400 diameters, they n to consist of flattened ovate granules, which in the same are tolerably uniform in size, but which vary in magnitude rent species of plants, those of the *canna*, or *tous les mois*,

Fig. 358.

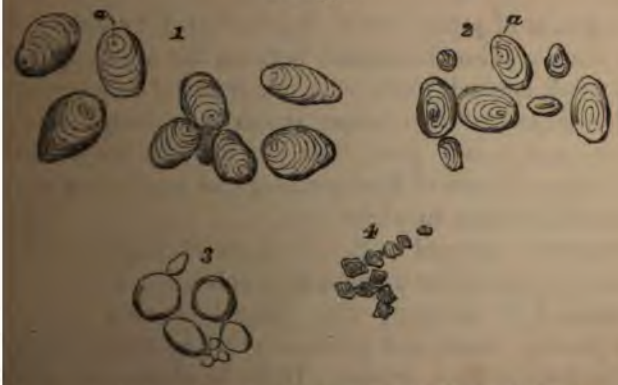

fig. 358, being about $\frac{1}{300}$th of an inch in diameter; those potato are somewhat smaller, but the grains become larger as the age of the plant increases; those of the arrow-root, No. 2, do not exceed $\frac{1}{600}$th of an inch; those of wheat starch, No. 3, are more circular, and about $\frac{1}{1000}$th of an inch in diameter, and do not exhibit rings; those of rice, No. 4, are angular and often adherent to each other; they do not usually exceed the $\frac{1}{3000}$th of an inch, whilst those contained in the cells of the beet-root are still smaller.

Each of the larger grains exhibits a series of concentric rings; some observers consider this appearance to indicate that they have been formed by a deposition of successive layers of starchy matter within an external envelope; Busk believes that the rings are occasioned by a plication of the envelope itself: in many instances the *hilum*, or supposed point of attachment of the grain to the cellular tissue of the plant from which it was developed, is distinctly perceptible, as shown at *a*, *a*, fig. 358.

The structure of the grains of starch is very beautifully displayed by placing some of them in contact with a drop of concentrated solution of chloride of zinc (tinged with a little free iodine), on the field of the microscope. No change takes place in the granules until a little water is added. They then become of a deep blue colour, and gradually expand; at first a frill-like plicated margin is developed around the globule; by degrees this opens out; the plications upon the globule may then be seen slowly unfolding, and may be traced in many cases into the rugæ of the frill; ultimately the granules swell up to 20 or 30 times their original bulk, and present the appearance of a flaccid sac. During these changes no extrusion of anything within the granules is observed to take place (Busk, *Quart. Jour. Microscopical Society*, vol. i.).

The grains of potato starch, if illuminated by polarized light, with a Nicol's prism interposed between the object and the eye, present a well-marked black cross, the centre of which corresponds with the hilum. When wheat starch is subjected to a similar test, this cross is not perceptible; its presence may therefore be of service as a means of distinguishing the fraudulent addition of potato starch or flour to wheat flour.

Properties.—As sold in the shops, starch exhibits the appearance of a white glistening powder, or of columnar masses which are easily reduced to powder; when pressed between the fingers it emits a peculiar sound, and produces a certain feeling of elasticity. Starch is heavier than water. It is insoluble in cold water, alcohol, and ether. If placed in a solution of soda or of potash, which contains 2 per cent. or upwards of alkali, the granules of starch swell up and become converted into a tenacious paste. A mixture of starch and water may be preserved without alteration at ordinary temperatures for an indefinite period; but it undergoes a remarkable change when heated to a temperature a little above 140° F. Under these circumstances the exterior layer of the granules absorbs water, the grains swell up, and the mixture suddenly assumes a viscous, pasty condition, in which form it is extensively employed by laundresses for stiffening linen. If this paste be largely diluted with water, the swollen granules of the starch slowly subside, whilst a certain quantity of amylaceous matter remains in solution. The starch paste thus obtained does not, when evaporated, recover its former insolubility. Its solutions are precipitated by alcohol, and the precipitate may be redissolved by the immediate addition of water; but after a few hours the flocculi become more coherent and are no longer soluble in cold water. A solution of starch produces right-handed rotation of a polarized ray.

It is remarkable, that if starch be boiled under pressure, at about 300°, with from 5 to 15 times its weight of water, a thin solution is obtained, which may be filtered from the insoluble portion; this liquid, as it cools, deposits minute spherical granules, which, when dried, have the whiteness of starch without its glistening appearance. These granules are sparingly soluble in cold water, but are readily dissolved when the water is raised to 158° or upwards. Iodine tinges them blue, and alcohol causes a precipitate when added to their aqueous solution.

When dry starch is heated sufficiently, it becomes soluble in cold water, and forms a ropy solution much resembling gum in properties. The grains of anhydrous starch may be heated to 320° without becoming soluble, but at 400° the change is complete in the course of an hour or two. Commercial starch, on the contrary, from the water which it retains, is rendered completely soluble by raising the temperature suddenly to 320°, and maintaining it at this point for some time. The change produced in these cases consists in the formation of a substance isomeric with starch, which is termed dextrin. This soluble torrefied starch is known under the name of *British gum,* and constitutes the *leiogomme* of the French manufacturers; it is largely employed by calico printers for mixing with their colours, in order to give them the requisite consistence.

Like most organized structures, starch appears to retain as an essential component a small quantity of saline matter, consisting partly of potash; and it likewise contains a perceptible amount of some azotised compound, which is present chiefly in the tegument of the grains (Jacquelain).

A solution of tannic acid occasions a precipitate in one of starch. When a dilute solution of starch is mixed with one of the ammoniacal acetate of lead, an insoluble compound with oxide of lead ($C_{12}H_9O_9,2\,PbO$) is formed. Starch may be recognised when present, by the deep blue colour which it acquires on the addition of free iodine to its solution; this colour disappears if the solution be heated, but it reappears as the liquid cools (331). If boiled with diluted sulphuric acid, starch quickly loses its viscidity, and is ultimately converted into glucose. Before the transformation is complete, it passes through the same modification that exists in British gum, which has received the name of dextrin, from its property of causing the rotation of a polarized ray from left to right. A solution of starch does not ferment with yeast; but Berthelot obtained as much as 16 per cent. of its weight of alcohol, when it was exposed for several weeks at a temperature of 100° F. in contact with chalk and cheese: no sugar could be detected in the liquid during this process; probably because it was decomposed as fast as it was formed.

Preparation.—In the extraction of starch from the vegetables in which it is contained, advantage is taken of its insolubility in cold water.

1. *Potato Starch.*—This variety is prepared on a large scale from potatoes, which contain about 20 per cent. of amylaceous matter; the cellular tissue of the tuber does not exceed 2 per cent. of the mass, whilst of the remainder, about 76 per cent. consists of water, and the rest of small quantities of sugar, salts, and azotised matters.* In order to extract the starch, the tubers are first freed from adhering earth by a thorough washing, and are then rasped by machinery. The pulp thus obtained is received upon a sieve, and is washed continuously by a gentle stream of water, so long as the washings run through milky. This milkiness is due to the granules of starch which are held in suspension.

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* The following, according to Boussingault, is the average composition of the tubers of the potato:—

	Moist.	Dry.
Water	75·9	
Albumen	2·3	9·6
Oily Matter	0·2	0·8
Fibre	0·4	1·7
Starch	20·2	83·8
Salts	1·0	4·1
	100·0	100·0

The milky liquid is received into vats, in which the amylaceous matter is allowed to subside; the supernatant water is drawn off, and the deposit is repeatedly washed with fresh water until the washings are no longer coloured. The starch is then suspended in a small portion of water, run through a fine sieve to keep back any portions of sand, and after having been again allowed to settle, is drained in baskets lined with ticking: the mass is then placed upon a porous floor of half-baked tiles, and dried in a current of air, which is at first of the natural temperature; the drying is completed by the application of a moderate artificial heat.

2. *Wheat Starch.*—A finer species of starch is obtained from the grains of the *Cerealia*, in the preparation of which wheat is largely employed. In making wheat starch a more complicated process is necessary, for in this grain the starch, which amounts to nearly 60 per cent. of the whole, is accompanied with an azotised material termed gluten (967), amounting to from 14 to 19 per cent. of the weight of the grain, which also contains a certain quantity of cellular tissue and of sugar. The grain is first coarsely ground and wetted with water. After the lapse of three or four days it begins to ferment, and is then transferred to a large vat where it is mixed with an additional quantity of water, and the fermentation is allowed to proceed for three or four weeks. During this operation the gluten undergoes putrefaction, the sugar and part of the starch become converted into alcohol, and carbonic acid is evolved, while the fermenting mass emits a powerful putrescent odour. A portion of the alcohol and of the starch become converted into acetic and lactic acids, which dissolve that portion of the gluten that has escaped putrefaction, and thus the starch is separated from the materials by which it was accompanied in the grain. It is then repeatedly washed, drained, and dried, as before. The blocks into which it is divided in order to facilitate the desiccation, shrink during the drying into columnar fragments, which are readily pulverized by gentle pressure.

3. *Rice Starch.*—In the foregoing method of preparing starch from wheat, much of the amylaceous matter is wasted, the whole of the gluten is lost, and the operation is attended with the continual evolution of gases of an offensive odour, which are the source of annoyance to the neighbourhood in which the manufacture is carried on. These inconveniences were overcome by Mr. O. Jones, who, in the year 1840, took out a patent for the manufacture of starch, by a method which he applied particularly to rice, though it may be used with other cereal grains. Un-

dried rice contains about 83 per cent. of starch, and about 7·0 per cent. of gluten. The process of Mr. Jones consists in separating these two materials by means of a very weak solution of alkali, which dissolves the gluten, but leaves the starch granules unaltered:—100lb. of rice in the form of grain are macerated in 50 gallons of a solution containing $\frac{1}{350}$th of its weight of caustic soda; after the lapse of 24 hours the alkaline liquid is drawn off, and the rice is allowed to drain; a fresh portion of alkaline ley is gradually added whilst the rice is being ground into a paste. It is then digested in the ley for 24 hours longer, with frequent agitation; at the end of that time the fibrous matter of the grain, which is heavier than the fine grains of starch, is easily freed from the latter, by stirring up the whole with water, allowing the mixture to rest for an hour, during which time the vegetable fibre subsides, and then running off the milky liquid into a separate vessel, where the starch is deposited; finally the starch is washed, mixed with a little smalt, to give it the blue tinge preferred in the market, drained, and dried in the usual manner. The liquid which floats above the starch is turbid, has a yellow colour, and contains the gluten of the grain in solution. From this liquid the gluten may be recovered by carefully neutralizing the solution with sulphuric acid. Starch, in the form in which it is usually sold, retains about 18 per cent. of water. In order to render it anhydrous, it should be dried *in vacuo*, at a temperature of 260°.

Other sources of Starch.—If, during the preparation of starch, the temperature employed in its desiccation be raised to 140°, a transparent jelly is produced, which, when dry, is no longer farinaceous, but assumes the form of semitransparent granules. *Sago* is the fecula obtained from the pith of the sago palm by making it into a paste with water, and pressing the mixture through a perforated metallic plate; the little cylinders thus obtained are granulated by placing them in a revolving vessel: these are then exposed upon a sieve to a jet of steam, and subsequently dried. *Tapioca* is the starch of the *Jatropha manihot*, which is pressed through a colander, and dried upon a metallic plate heated to 212°. It is thus formed into granular, semitransparent, irregular masses. *Arrow root* is the starch of the root of the *Maranta arundinacea*, and of one or two other tropical plants. *Salep* is the name given to that yielded by the *Orchis mascula*.

The occurrence of starch has been supposed not to be confined to the vegetable kingdom. Granules of a substance, which, after being moistened with oil of vitriol, becomes blue on the addition of iodine, have been found in the brain; in certain cases of scrofulous caries the liver assumes the peculiar hard, semitransparent, waxy appearance, described by Dr. G. Budd, and a similar deposit has been found in the kidney in the same cases. The deposition of small quantities of this material in the animal tissues, even in health, is not uncommon. This compound is, however, not true starch, but is azotised in composition. It does not yield sugar when heated with acids, or any of the characteristic products of starch.

(947) *Diastase.*—During the germination of seeds the starch undergoes a species of fermentation, and is converted into a mixture of dextrin and sugar, in which state it is assimilated by the young shoot. This conversion is due to the action of a peculiar ferment termed *diastase*, which exists in all germinating seeds during the act of growth, being probably merely albumen or gluten in a particular stage of decomposition. An impure solution of diastase may be readily obtained from malt or freshly-germinated barley by grinding it, moistening it with half its weight of warm water, allowing it to stand for a few minutes, and pressing out the liquid. Malt does not contain more than $\frac{1}{500}$th of its weight of diastase. One part of this substance suffices to convert 2000 parts of starch into dextrin and sugar (Persoz and Payen); the temperature of 150° F. is most favourable to the change; the diastase is coagulated at about 170°, above which point this conversion is arrested.

Long before the discovery of diastase, the distillers had found that by mixing a portion of unmalted barley with their malt, and digesting the mixture in warm water for some hours, they obtained an infusion or wort equally sweet with that furnished by an equal weight of malt: 1 part of malt having the power to change into dextrin and sugar the starch contained in 4 or 5 parts of barley. Now unmalted barley contains but very little sugar, whereas after it has been malted the proportion of sugar is much increased, whilst that of the starch is diminished. Malt is simply barley allowed to germinate up to a certain point, after which its growth is suddenly checked by the application of heat; and it contains a considerable quantity of diastase which has not been expended in the conversion of its starch into sugar. When the mixture of ground malt and barley is digested with water, or *mashed,* this excess of diastase acts upon the starch of the unmalted barley, converting it into a mixture of dextrin and sugar;* a saccharine liquid is thus obtained which is susceptible of fermentation. The preparation of such a sweet wort is the first step in the process of brewing. In malted barley this saccharification of the starch has already taken place during the act of germination, and simple digestion in water extracts the sugar. But since raw barley is less expensive than malt, a certain quantity of it is often substituted for a portion of the germinated grain by the distiller, who sometimes adds as much as 4 parts of unmalted grain to 1 of malt, and thus effects a considerable pecuniary saving.

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* Musculus has shown (*Ann. de Chimie,* III. lx. 203) that only one-third of the starch undergoes this conversion into sugar, two-thirds remaining in the form of dextrin. In the preparation of sweet wort for the distiller, it is therefore much more economical to treat unmalted barley with diluted sul-

(948) *Action of Ferments.* — The exact manner in which diastase acts in producing this singular change is unknown, and the same may be said of the mode in which sugar is converted into alcohol and carbonic acid through the intervention of yeast. These actions, however, exhibit considerable analogy with each other, and are connected in some way with the decomposition of the matter serving as a ferment. Moist yeast and moist diastase both very rapidly undergo alteration. Diastase, when in a state of decomposition, however, produces changes on other matter entirely distinct from the transformation of starch into dextrin; and an examination of these changes has thrown considerable light on the obscure subject of ferments in general.

It has already been stated that if starch be acted on for some time by diastase, it is partially converted into sugar, but in a certain stage of its decomposition diastase may give rise to products of a different kind :—An infusion of malt if kept for a few days converts the starch into gum instead of into sugar; at other times mannite is formed; in other cases the starch is converted first into sugar, and this compound is then rapidly transformed into lactic acid; whilst the same infusion, at a still later period of its decomposition, becomes turbid, and acquires the power of exciting the alcoholic fermentation. These observations indicate that the same body during its different states of decay may give rise to the formation of products quite different in properties from each other, though all these products, except mannite, have the same ultimate composition. Hence it has been concluded, that the formation of each of these compounds corresponds to a particular phase of decay in the ferment, attended, probably, with the development of fungi or organisms of a kind varying, in each particular stage, with the products obtained: and it has been

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phuric acid, and boil (938), so as to change the whole of the starch into glucose. The acid can then be neutralized with chalk, and the liquid, strained from the husks, can afterwards be fermented and distilled as usual.

supposed that the molecular constitution of all bodies in contact with a ferment, provided that they be susceptible of change, undergoes alterations definite in their nature, and dependent upon the peculiar mode of decomposition which the ferment is itself experiencing. If this explanation be admitted, it is easy to see why in many instances the products of fermentation are of a more or less mixed nature, according as the ferment itself has passed through more or fewer phases of its decomposition.

All substances susceptible of putrefactive decomposition—such as casein, albumen, mucous membrane, muscular tissue, and the albuminoid azotised principles of plants—may act as ferments: that is, they may induce decomposition of a particular kind, in bodies—like sugar, starch, urea, and various others—which undergo no change unless some agent susceptible of putrefaction be employed. All these azotised putrescible substances possess certain properties in common whilst they are undergoing putrefaction; but each of them is susceptible of certain phases of decomposition peculiar to itself. For example, the synaptase of the almond (1241) acts upon starch and sugar in a way resembling that in which yeast and gluten act, converting starch into sugar, and sugar into alcohol and carbonic acid; but it has, in addition, the peculiar property, not possessed by yeast or gluten, of converting amygdalin into hydrocyanic acid and essential oil of bitter almonds, and also of changing salicin into saligenin and sugar (1271).

The observations of Schröder (*Liebig's Annal.* cix. 35, and cvii. 273) upon the processes of fermentation and putrefaction are remarkable. He has shown that any organic liquid may be prevented from fermenting or putrefying, if it be heated under pressure to about 266°, then transferred to a flask and boiled, the mouth of the flask being plugged whilst boiling with a pellet of cotton wool. In this way he preserved, during a hot summer, various liquids, including freshly boiled wort, blood, white of egg, whey, urine, broth, and milk; but when afterwards the plug of cotton was withdrawn, these liquids in a few days began to undergo decomposition. He explains these results by supposing that the spores of some organism must find access to the substance in order to set up the process of decomposition; by a temperature of 260° any such spores which the substance itself might contain are destroyed, and as the air is filtered through the cotton before it reaches the interior of the flask, none of these organic germs can afterwards obtain access to the body under experiment. I have repeated some of these experiments with complete success.

(849) *Preparation of Malt.*—Upon the proper management of

the process of malting much of the success of the subsequent brewing depends. The seasons most favourable for malting are spring and autumn, when the temperature is neither very high nor very low. The barley first undergoes the operation of steeping. This is effected in stone troughs, where the grain is covered with water to a depth of about 6 inches. The lighter and decayed seeds float, and are skimmed off, whilst the sound grain, being heavier than the water, subsides. The steeping is continued until the grain becomes uniformly soft, and this occupies generally from 40 to 60 hours, the water being changed twice or thrice. During this stage, the barley swells considerably from the moisture which it imbibes, and increases in weight nearly one-half. After a final washing it is drained and then *couched*, or placed in heaps of about 15 inches in height upon the floor. In these heaps it becomes warm, and continues to swell for the next twenty-four hours: by this time it begins to sprout; as soon as the first whitish protuberance shows itself, the heaps are evenly distributed over the floor of a darkened apartment, and the process termed *sweating* follows. In this state it is allowed to remain several days, usually fourteen; the workmen turning it twice or thrice daily with wooden shovels. This step is employed for the purpose of equalizing the heat, in order that the process of germination may proceed at all points with equal rapidity. By this manipulation the temperature is maintained at a point varying between 55° and 62°. In from 10 to 20 days, according to the heat of the weather, the germination is complete; and as soon as the radicle or *acrospire*, as the maltster calls it, has shot to the length of about half an inch, when it bifurcates, and just as the plumula or leaf-shoot is about to make its appearance, the vitality of the seed is extinguished by rapidly drying the grain. In order to effect this object, the malt is spread, to the depth of about 2½ inches, upon floors made of perforated metallic plates. Here it is left to dry in a current of air for some hours, at a temperature not exceeding 90°; at the end of this time a fire is lighted underneath. It is necessary that the greater part of the moisture be expelled before the fire be kindled; afterwards the heat is allowed to rise gradually, but not to exceed 140°, otherwise the starch of the grain would be acted on, and much of the diastase would lose its efficacy. *High dried* malt is subjected to a much higher temperature, and is actually scorched on the outside. Such malt, however, is used only in small quantity as a colouring ingredient, to give the customary deep brown tinge to *porter*. During the drying, which occupies ree days, the grain requires frequent stirring, in order desiccation may take place regularly. Barley generally out 80 per cent. of malt after drying and sifting from the According to Thomson, 12 per cent. of this loss is due ; only 8 per cent. being actually wasted in the form of acid and trimmings. During the germination, oxygen is and a large quantity of carbonic acid is set at liberty. ins, such as wheat, oats, rye, and even Indian corn, may l, but experience has shown that barley is the grain best o this process. It yields the largest quantity of diastase, this does not exceed $\frac{1}{500}$th of the weight of the grain. ase appears to be developed at the expense of the azotised ts of the grain. It is generated chiefly in the neighbourhood of the young germ, not of the rootlet.

ding to the experiments of Lawes, 100 parts of dry ld 90·22 of malt, and 3·99 of malt and kiln dust. It is e that the malt dust, consisting chiefly of the radicles of carries off with it a great deal of the nitrogen of the ounting to nearly one-ninth of the entire quantity con- the barley. The loss in nitrogen which barley suffers ng converted into malt rises to as much as 13·5 per cent. l quantity of nitrogen contained in 100 parts of dry Lawes found the nitrogen in the barley to amount to cent. of the weight of the dry grain; that contained in being 1·70 per cent.

Dextrin ($C_{12}H_{10}O_{10}$) is a transparent, brittle solid, with fracture. It is soluble in water and in dilute alcohol, soluble in anhydrous alcohol or in ether; wood spirit it freely. Dextrin is distinguished by producing right- tation upon a ray of polarized light, and it derives its name property. It differs from starch in not yielding any ation with iodine; and from gum by the fact that a f dextrin, when mixed with potash, forms a beautiful blue n the addition of sulphate of copper, which, on boiling, boxide of copper; whilst no such effect is produced with is not susceptible of fermentation. Nitric acid converts to oxalic, not into mucic acid. Payen has contrived a f preparing dextrin on a large scale, which consists ing 10 parts of starch with 3 of water containing $\frac{1}{150}$th t of nitric acid, allowing the mixture to dry spontaneously, ding the starch upon shelves in layers of an inch and depth, and heating them for an hour or an hour and a-half in an oven to about 240°. Dextrin is likewise largely manufactured in a more strongly coloured form by heating starch to about 400° (p. 99), when it yields British gum. It may also be obtained by heating an infusion of ground malt in water to 165°, and adding starch in small quantities at a time; as soon as the starch is dissolved the liquid is rapidly heated to 212°, filtered, and evaporated, with constant agitation, until it has acquired a syrupy consistence. When a solution of dextrin is mixed with one of ammoniacal basic acetate of lead, it forms an insoluble precipitate consisting, according to Payen, of 2 $PbO,C_{12}H_{10}O_{10}$.

(951) INULIN ($C_{24}H_{21}O_{21}$; Parnell).—The roots of many plants, among which are those of the dahlia, elecampane (*Inula helenium*), colchicum, dandelion, and chicory, contain a variety of starch, to which the name of *inulin* has been given. It is a white, pulverulent, inodorous, tasteless powder, insoluble in alcohol, sparingly soluble in cold water, but readily so in boiling water, from which it is deposited again on cooling in a pulverulent form. Its solution produces left-handed rotation upon a ray of polarized light. By long boiling it assumes the characters of gum. If heated beyond 212° it melts, gives off water, and leaves a scaly, sweetish, gummy mass, which is readily soluble in water. Iodine turns inulin yellow. By boiling with dilute acids it is converted first into dextrin, and then into grape sugar. If heated with nitric acid in the concentrated form, it is converted into oxalic acid. It forms an insoluble precipitate when its solution is mixed with one of acetate of lead and ammonia is added. In this manner Parnell obtained two different compounds, which when dried at 212° contained, $C_{24}H_{18}O_{18},3\ PbO$, and $C_{24}H_{21}O_{21},5\ PbO$.

(952) GUM is found in the juices of almost all plants, but is met with in its purest form in transparent tears, which exude from various species of acacia. Gum arabic may be taken as its type. This variety of gum is frequently described under the name of *Arabin* ($C_{12}H_{11}O_{11}$). It is soluble in water, forming a tasteless, ropy, mucilaginous liquid, which from its adhesive quality often forms a useful substitute for paste or glue. A solution of gum arabic produces left-handed rotation of a polarized ray. It is not susceptible of the alcoholic fermentation under the influence of yeast; but, if digested with cheese and chalk, it may be made to furnish alcohol, which amounted, in one experiment, to 12 per cent. of the gum employed: lactate of lime is formed at the same time, but no formation of sugar is perceptible (Berthelot). A solution of arabin is precipitated by alcohol and by ether in white

flocculi, or, if dilute, in the form of a milky turbidity. If boiled with dilute sulphuric acid, it is gradually converted first into dextrin, and then into a fermentable variety of sugar; concentrated nitric acid converts it into mucic and oxalic acids, showing its relation to sugar of milk in this respect: iodine does not alter its colour. It forms soluble compounds with the alkalies and alkaline earths; a solution of gum is not precipitated by admixture with solutions of alum, protochloride of tin, the persalts of iron, sulphate of copper, or nitrate, or neutral acetate of lead; but when mixed with one of ammoniacal acetate of lead it produces a curdy precipitate ($PbO,C_{12}H_{11}O_{11}$). Some other metallic salts, such as the nitrates of the grey and red oxide of mercury, also precipitate its solution, and the precipitate is redissolved by an excess of the metallic salt. *Mucilage* or *bassorin* ($C_{12}H_{10}O_{10}$) is a modification of gum which is insoluble in water; but, when moistened with this liquid it swells up into a gelatinous mass. It is contained abundantly in gum tragacanth, and accompanies the gum which exudes from the cherry tree. Many seeds, such as linseed, quince-seed, and certain roots, such as those of the marsh-mallow, furnish it in large quantity: alkalies render it soluble in water, and convert it into true gum; long boiling in water has a similar effect. Nitric acid converts it into mucic and oxalic acids. Bassorin, as contained in an infusion of linseed, is precipitated by alcohol, nitrate of suboxide of mercury, corrosive sublimate, and by neutral acetate, and subacetate of lead.

The various kinds of mucilage from different plants, however, present some differences in their reactions;—thus, quince-seeds give a mucilage which yields oxalic acid only, when treated with nitric acid; moreover, it is coloured blue when moistened with oil of vitriol containing iodine, and a solution of iodine in iodide of zinc produces in a few days a beautiful red tint; the mucilage of linseed is not so coloured by either of the agents last named.

(933) VEGETABLE JELLY (formerly called *pectin*).—Another principle which, like starch and gum, extensively pervades the vegetable kingdom, is that peculiar body which gives to the juice of many succulent fruits and roots the faculty of gelatinizing. Braconnot first called attention to this substance under the name of *pectin*; it has since been particularly studied by Mulder and by Chodnew; and by Fremy (*Ann. de Chimie*, III., xxiv. 5) especially in relation to the ripening of fruits.

According to the last-mentioned chemist, the cellular tissue of green fruits, and of turnips, carrots, parsnips, &c., contains a substance which he terms *pectose*, and which is quite insoluble in water, alcohol, and ether. It is the material which gives hardness to green fruits, and it possesses the characteristic perty of becoming converted, under the influence of dilute a aided by a gentle heat, into pectin.

Pectin may be obtained from the juice of ripe pears or app by throwing down the lime which they contain by the cauti addition of oxalic acid, and then adding a concentrated solutio tannin so long as it occasions a precipitate; the albumen is coagulated, and may be separated by filtration. On adding alc to the clear liquid, the pectin is thrown down in the form gelatinous strings. If this precipitate be redissolved in cold w and again precipitated by alcohol, it may be obtained toler pure: when dry it forms a friable mass, which is soluble in w but insoluble in alcohol and in ether. Its aqueous solution is so what viscous: it gives a gelatinous precipitate when mixed basic acetate of lead, but none with the neutral acetate of metal. Pectin exerts no action on polarized light. When bo with water it loses its viscosity, and becomes converted int modification (*parapectin*), which occasions a precipitate in a solu of neutral acetate of lead. If boiled with dilute acids, an isom substance (*metapectin*) is formed, which occasions a precipi when mixed with a solution of chloride of barium, even if liquid be somewhat acid.

Pectic acid ($2\,HO,C_{32}H_{20}O_{28}$; Fremy).—All the above modi tions of pectin are rapidly converted into pectic acid by being tre with a solution of a caustic alkali, or of an alkaline carbonate, being taken to avoid any excess of the alkali. Pectic aci characterized by its gelatinous nature, whence, indeed, it de its name (from πηκτὶς, a jelly). It forms soluble compounds the alkalies, but they do not crystallize; the other pectates insoluble. Pectic acid is likewise soluble in many of the sal the alkalies. It is most easily obtained by boiling the washed of carrots or turnips in a weak solution of carbonate of s pectate of soda is thus formed by the action of the alkali the insoluble pectose contained in the vegetable tissue; an mixing the solution with chloride of calcium, a gelatinous pe of lime is precipitated. This when well washed and treated dilute hydrochloric acid, to remove the lime, furnishes pectic as a transparent insoluble jelly.

If this jelly be long boiled with water it is gradually disso and a deliquescent uncrystallizable acid is the result (*parap acid*), which yields a precipitate with chloride of barium. pectic acid in its turn, when treated with alkalies, passes another uncrystallizable acid, the *metapectic*, which has a str ur taste; it is no longer precipitable by chloride of barium, though yields a precipitate with subacetate of lead.

According to Fremy, pectin is susceptible of a specific fermen-ion, produced by a peculiar substance which is present in the lular tissue of the vegetable. This change is not attended by disengagement of gas, but simply by the conversion of the ble pectin into two gelatinous acids, which are insoluble in er: one of these acids he terms *pectosic acid*. It is almost luble in cold water, but becomes dissolved by boiling water, the liquid gelatinizes on cooling. This acid appears to be one formed in the first instance, but it gradually passes into cond, which is the pectic acid already described; the gela-ing of many juices of fruits arises from the gradual con-on of the pectin which they contain into these gelatinous . The composition of these gelatinous bodies cannot be said established with certainty; since there is no means of deter-ng whether or not they have been prepared in a pure condition, is it easy to procure them in a uniform state of desiccation. whatever may be the true composition of these bodies, it is that pectose is readily susceptible of modification under the ence of acids, of alkalies, and of a peculiar ferment contained e plant or fruit itself; and these modifications are probably ected with the assimilation or separation of the elements of r. None of these compounds exert any rotatory action upon ized light, a character which indicates an important molecular ction between them and the class of sugars. All these ly related bodies, it may be observed, contain oxygen in larger rtion than would be required to convert their hydrogen into r. When treated with nitric acid they furnish mucic and c acids.

Fremy assigns to these different bodies the composition given he following table, but the formulæ require confirmation:—

Pectose	Composition unknown.	Not gelatinous.
Pectin	$C_{64}H_{40}O_{56}+8\,HO$	Viscous.
Parapectin	$C_{64}H_{40}O_{56}+8\,HO$	Not gelatinous.
Metapectin	$C_{64}H_{40}O_{56}+8\,HO$	Not gelatinous.
Pectosic Acid . . .	$2\,HO,C_{32}H_{20}O_{28}+\ HO$	Gelatinous.
Pectic Acid	$2\,HO,C_{32}H_{20}O_{28}$	Gelatinous.
Parapectic Acid . .	$2\,HO,C_{24}H_{15}O_{21}$	Not gelatinous.
Metapectic Acid . .	$2\,HO,C_8\,H_5\,O_7$	Not gelatinous.

§ IV. CELLULIN AND WOODY FIBRE.

54) **CELLULIN**, or **CELLULOSE** ($C_{36}H_{30}O_{30}$).—If a thin slice od be examined under the microscope, it is immediately

water, alcohol, and ether. It is the material which gives hardness to green fruits, and it possesses the characteristic p perty of becoming converted, under the influence of dilute ac aided by a gentle heat, into pectin.

Pectin may be obtained from the juice of ripe pears or appl by throwing down the lime which they contain by the cautio addition of oxalic acid, and then adding a concentrated solution tannin so long as it occasions a precipitate; the albumen is th coagulated, and may be separated by filtration. On adding alcoh to the clear liquid, the pectin is thrown down in the form gelatinous strings. If this precipitate be redissolved in cold wate and again precipitated by alcohol, it may be obtained tolerabl pure: when dry it forms a friable mass, which is soluble in wate but insoluble in alcohol and in ether. Its aqueous solution is som what viscous: it gives a gelatinous precipitate when mixed wi basic acetate of lead, but none with the neutral acetate of th metal. Pectin exerts no action on polarized light. When boil with water it loses its viscosity, and becomes converted into modification (*parapectin*), which occasions a precipitate in a soluti of neutral acetate of lead. If boiled with dilute acids, an isomer substance (*metapectin*) is formed, which occasions a precipita when mixed with a solution of chloride of barium, even if th liquid be somewhat acid.

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etapectin	$C_{64}H_{40}O_{56}+8\,HO$	Not gelatinous.
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§ IV. Cellulin and Woody Fibre.

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According to Fremy, pectin is susceptible of a specific fermentation, produced by a peculiar substance which is present in the cellular tissue of the vegetable. This change is not attended by any disengagement of gas, but simply by the conversion of the soluble pectin into two gelatinous acids, which are insoluble in water: one of these acids he terms *pectosic acid.* It is almost insoluble in cold water, but becomes dissolved by boiling water, and the liquid gelatinizes on cooling. This acid appears to be the one formed in the first instance, but it gradually passes into a second, which is the pectic acid already described; the gelatinizing of many juices of fruits arises from the gradual conversion of the pectin which they contain into these gelatinous acids. The composition of these gelatinous bodies cannot be said to be established with certainty; since there is no means of determining whether or not they have been prepared in a pure condition, nor is it easy to procure them in a uniform state of desiccation. But whatever may be the true composition of these bodies, it is clear that pectose is readily susceptible of modification under the influence of acids, of alkalies, and of a peculiar ferment contained in the plant or fruit itself; and these modifications are probably connected with the assimilation or separation of the elements of water. None of these compounds exert any rotatory action upon polarized light, a character which indicates an important molecular distinction between them and the class of sugars. All these closely related bodies, it may be observed, contain oxygen in larger proportion than would be required to convert their hydrogen into water. When treated with nitric acid they furnish mucic and oxalic acids.

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§ IV. CELLULIN AND WOODY FIBRE.

(954) **CELLULIN**, or **CELLULOSE** ($C_{36}H_{30}O_{30}$).—If a thin slice of wood be examined under the microscope, it is immediately

apparent that it is not a homogeneous structure, but that composed of a cellular or fibrous substance, the texture of assumes a different appearance, according as the slice ha cut across the grain of the wood, or parallel to it. This li fibre, or true woody matter, consists, according to the resear Payen, of two essentially distinct portions. One of these, wh received the name of *cellulose*, which it is better to change into reserving the termination *ose* for the different varieties of is the basement tissue, found in all vegetables; it is near in cotton, linen, elder pith, and in the pith of the *Aralia fera* (Hooker), from which *rice paper* is prepared; the other is a deposit of incrusting matter which lines the interior cellules in amorphous layers, varying in thickness accordin age or character of the ligneous substance.

Cellular tissue forms the groundwork of every plant, an obtained in its pure state, its composition is the same, w may have been the nature of the plant which furnished it, it may vary greatly in appearance and physical characters; is loose and spongy in the succulent shoots of germinatin and in the roots of plants, such as the turnip and potat porous and elastic in the pith of the rush and the elde flexible and tenacious in the fibres of hemp and flax; it pact in the branches and wood of growing trees, and it very hard and dense in the shells of the filbert, the pea cocoa-nut, and the *Phytelephas*, or vegetable ivory. Ve cellular tissue, in its succulent form, is easily digestible, but it has become compact and incrusted with true woody ma in the husks of the seed, and in the hard portions of the and even when simply condensed into tenacious fibres, lik of hemp and flax, it is no longer digestible, or in a condi serve as nutriment to the higher orders of animals.

It is scarcely possible to obtain cellulin free from l tissue by artificial means, since the incrusting woody matte once deposited within its meshes, is retained with great ob but it is presented in a pure condition in finely carded co linen, and in the finest kinds of filtering paper; to these the chemist usually has recourse when he desires to exam properties of cellulin.

Pure cellulin is a white, tasteless substance, insol water, alcohol, ether, or oils. It is heavier than water: it are transparent, and exert a depolarizing influence upon a polarized light. A solution of oxide of copper in a dissolves the fibre in most of its forms, though in some c in that of the *rice paper*, this solution does not take place until it has been boiled with diluted acids. Cellulin is precipitated from the cupric solution, unaltered in composition, on acidulating the solution with an acid. Cold concentrated sulphuric acid dissolves it, and produces a treacly liquid, converting it, after dilution and boiling, first into dextrin, and subsequently into grape sugar. Weak acids exert but little effect upon cellulin, but the action of these and of all other solvents is materially greater upon the recently formed cellules than upon the old ones. Hydrochloric acid, in its concentrated form, dissolves cellulin, and deposits it on immediate dilution with water; but if it be left undiluted for 2 or 3 days, no precipitate occurs on the addition of water. Alkaline liquids when dilute do not act upon cellulin, but when concentrated they gradually destroy its texture. A solution of chlorine acts but very slowly upon cellulin.

Cellulin, in its natural state, is not coloured blue by iodine; but after it has been digested for a short time with sulphuric acid, it becomes of a fine blue when free iodine is added. This reaction is sometimes serviceable in the microscopic examination of vegetable tissues; cellulin being thus easily distinguished from most tissues into the composition of which nitrogen enters. By the prolonged action of sulphuric acid, the property of being coloured blue by iodine disappears, the dextrin and sugar which are formed not being susceptible of the blue coloration.

A remarkable modification in the vegetable fibre is effected by the action of chloride of zinc or of sulphuric acid, in consequence of which paper may be converted into a material, which, in toughness and appearance, much resembles parchment, and is known under the name of *vegetable parchment*. It is more transparent than true parchment. In order to prepare it, thin paper, which must not be sized, is plunged for a few moments, at a temperature of 60°, into a mixture of oil of vitriol with half its bulk of water. The paper must be quickly withdrawn and washed, first with water, then with a weak solution of ammonia, and, lastly, with water again. In this process the outer surface of the fibres appears to have become converted into a glutinous substance by which the fibres are cemented together. This substance, according to Hofmann, is intermediate between cellulin and dextrin, with both of which it is isomeric, having neither acquired nor given up the elements of water, nor entered into permanent combination with sulphuric acid.

Hofmann found the toughness of this vegetable parchment to be five times as great as that of the *paper which furnished* it, and

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and a mixture of nitrate and nitrite, as well as of oxalate of potash. The solution in potash contains a peculiar acid (resembling the saccharic), which yields an insoluble precipitate with acetate of lead. The alkaline solution of pyroxylin, when mixed with ammonia-nitrate of silver, and gently heated, reduces the silver in the form of a film upon the surface of the glass, producing a brilliant mirror-like surface.

Strong sulphuric acid dissolves pyroxylin in the cold without the evolution of gas, and the liquid is not rendered turbid by dilution. If the pyroxylin be pure, the solution is colourless, but it is brown if any unaltered fibres of cotton remain in the mass. Nitric acid in the cold is without action upon it, but if the acid be heated, it gradually dissolves the pyroxylin, and on dilution deposits it again. By boiling it with the acid it is decomposed, red fumes escape, and dilution then causes no precipitate. Pyroxylin, according to the observation of Hadow, may be reconverted into ordinary cotton, by digestion at ordinary temperatures in an alcoholic solution of hydrosulphate of potassium (KS,HS), whilst nitrite of potash is formed; and the change may be effected still more rapidly if the mixture be heated: the reaction may be indicated by the following equation:—

$$2\overbrace{(C_{36}H_{21},9\,NO_4,O_{30})}^{\text{Pyroxylin.}}+18\overbrace{(KS,HS)}^{\substack{\text{Hydrosulph.}\\ \text{Potas.}}}=2\overbrace{(C_{36}H_{30}O_{30})}^{\text{Cellulin.}}+18\overbrace{(KO,NO_3)}^{\text{Nitrite potash.}}+9\,S_4.$$

Béchamp states that a similar reduction takes place when the pyroxylin is acted upon by protochloride of iron.

The most remarkable property of pyroxylin is the facility with which it takes fire, and the rapid and complete manner of its combustion. In the open air it burns with a flash, but without either smoke or report; a temperature just below that of 400° is sufficient to inflame it, being nearly 200° less than that required to ignite gunpowder. In the open air, pyroxylin burns more rapidly than gunpowder, but if compressed so as to form a fusee, its rapidity of combustion may be reduced below that of powder, and the more it is compressed the slower is the combustion. If it be fired in a confined space it produces violent explosive effects from the suddenness of its combustion, and from the large quantity of gaseous matter which it furnishes. The extreme suddenness of its inflammation, and the short space of time during which its propulsive force is exerted, produce both greater strain upon the gun-barrel, and less effect upon the ball, in consequence of which it appears to be less eligible as a projectile agent than gunpowder. In certain cases, such as in mining operations in hard and brittle rocks, it may be beneficially employed, as it may be driven into borings above the head of the miner; and if mixed with nitre in quantity sufficient to convert the whole of the carbon into carbonic acid, it produces much less fume and noxious gases than gunpowder; in addition to which it has the great advantage of leaving no 'train' by leakage from the vessels in which it is stored up. This compound may be exposed to damp and even to prolonged immersion in water, and, if it be again dried, it will have experienced no diminution of its explosive power.

During the combustion of pyroxylin a large volume of steam is generated, mixed with a variable proportion of carbonic acid, carbonic oxide, and nitrogen gases; traces of nitric acid and of cyanogen are also formed. Considerable difference prevails in the statements of different experimenters respecting its propulsive power as compared with that of gunpowder: all agree that weight for weight its explosive force is much greater, some say three times as great, others four times that of the best musket powder. According to the experiments of a Commission appointed by the French Government to examine the question, the explosive power of the pyroxylin appears in some measure to depend upon the degree of compression to which the charge is subjected; as a mean result, the pyroxylin produced an effect equal to that of about three times its weight of gunpowder.

The results of Hadow's experiments, (*Q. J. Chem. Soc.* vii. 208), serve to explain the conflicting statements relative to the properties and composition of this remarkable substance. It appears from this inquiry that the composition of gun cotton differs according to the degree of concentration of the acids employed in its formation, and that at least four different and definite compounds, distinguished as A, B, C, and D, may be formed, having the following composition:—

$$A=C_{36}\left.\begin{matrix}H_{21}\\9\,NO_4\end{matrix}\right\}O_{30}; \qquad B=C_{36}\left.\begin{matrix}H_{22}\\8\,NO_4\end{matrix}\right\}O_{30};$$

$$C=C_{36}\left.\begin{matrix}H_{23}\\7\,NO_4\end{matrix}\right\}O_{30}; \qquad D=C_{36}\left.\begin{matrix}H_{24}\\6\,NO_4\end{matrix}\right\}O_{30}.$$

When equal measures of the sulphuric and nitric acids are employed, each in the highest degree of concentration, the compound A is formed: it is highly explosive, soluble in acetic ether, and insoluble in any mixture of alcohol and ether. If the acids used be of a strength intermediate between HO,NO_5 +

2 HO,S_2O_6+3 Aq, and $HO,NO_5+2\ HO,S_2O_6+4$ Aq, the compound B is produced: it is less explosive than A, is insoluble in acetic acid, but soluble in a mixture of seven parts of ether and one part of alcohol. Mixed acids of the strength $HO,NO_5+2\ HO,S_2O_6+4$ Aq, produce the compound C, which is largely soluble both in ether and in glacial acetic acid: it is highly combustible, but scarcely explosive. The compound D is formed when acids of the strength $HO,NO_5+2\ HO,S_2O_6+5$ Aq are used: it is but sparingly soluble in alcohol and ether and not soluble in boiling glacial acetic acid.

Collodion.—The solution of pyroxylin in a mixture of ether and alcohol is known under the name of *collodion*. When this solution is exposed to the air for a few moments in the form of a thin layer, the solvent evaporates, leaving the pyroxylin as a transparent membranous pellicle. Collodion has been applied to excoriated surfaces, for the purpose of forming an artificial skin in order to protect them from the action of the air; but its most extensive application is in the preparation of a sensitive transparent surface for the reception of photographic images (884), by diffusion over plates of glass, after it has been duly impregnated with a soluble iodide. On immersing the film in a solution of nitrate of silver, the whole surface becomes impregnated with iodide of silver in the most favourable condition for the reception of photographic impressions. According to Hadow, the compound B is that which is best fitted for the preparation of photographic collodion. The temperature at which the compound is formed, has a very material influence upon the mechanical qualities of the collodion. If the temperature be not raised to 120° or upwards, the solution is viscid and glairy, and does not diffuse itself readily over the glass. The successful preparation of a good photographic collodion requires attention to a number of minute precautions, which are detailed in Hardwich's *Manual of Photography*.

(956) *Nitrous Derivatives from Sugar, &c., allied to Pyroxylin.*—Other substances besides cellulin may be converted into bodies more or less analogous to pyroxylin, by the action of a mixture of nitric and sulphuric acids. Powdered cane sugar is converted by the same mixture of acids into a bitter yellowish mass of resinous appearance: it is very slightly soluble in water, and according to Sobrero contains $C_{12}H_9(NO_4)_2O_{11}$. A somewhat similar compound may be formed from gum arabic, and also from milk sugar. If starch be *treated with concentrated* nitric acid, it

is rapidly dissolved, and if the viscid solution thus obtained be immediately diluted with water, a white tasteless insoluble precipitate is occasioned, termed *xyloidin*, which appears to be a substitution-product of starch and peroxide of nitrogen, $C_{12}H_8(NO_4)_2O_{10}$, analogous to the foregoing: this substance by digestion in hydrosulphate of potassium (KS,HS), is reconverted into the soluble modification of starch, which becomes blue when mixed with iodine, whilst xyloidin does not yield a blue with iodine. But the most remarkable body belonging to this class is one which is produced when mannite is acted upon by the mixture of nitric and sulphuric acids. It is insoluble in water, but is readily dissolved by boiling alcohol; the *nitromannite* $[C_{12}H_8(NO_4)_6O_{12}]$ crystallizes in fine needles as the solution cools. This compound explodes powerfully by a blow from a hammer. If gently heated it may be melted, but at a higher temperature than that required for its fusion, it explodes, and produces red vapours.

In all these cases it will be observed that the derivative nitrous compounds are produced from the saccharine or amylaceous substance by the substitution of a variable number of atoms of hydrogen by an equal number of equivalents of peroxide of nitrogen; each atom of nitric acid, when acted upon by an atom of hydrogen derived from the organic body, yielding one equivalent of water and one of peroxide of nitrogen, whilst the basic water of the acid is separated; $HO,NO_5+H=NO_4+H_2O_2$. The water is absorbed by the sulphuric acid contained in the mixture, which, after its action upon the organic compound, is found in all cases to have become diluted by the water thus removed from the body submitted to its influence. The addition of the sulphuric acid in these cases has two advantages, one being the removal of the water produced by the reaction; the other, the prevention of the solution of the new compound, and its further alteration by the nitric acid. A mixture of nitric and sulphuric acids is now frequently employed for the purpose of obtaining compounds in which NO_4 is substituted for hydrogen: nitroglycerin ($C_6H_6(NO_4)_2O_6$; De Vry) and various other compounds may be obtained in this manner with facility; the reaction however requires careful watching, as it is apt to become tumultuously violent, and sometimes, as in the case of nitroglycerin, the compounds which are formed are liable to explode during their preparation.

(957) LIGNIN.—The incrusting matter contained within the cellular tissue, which gives hardness to wood, is most abundant in

art-wood of trees, and in the hard shells of many varieties
s. This substance appears to be a mixture of several proxi-
principles ; it contains a larger proportion of hydrogen than
n, the proportion of oxygen being insufficient to convert the
of the hydrogen into water. This incrusting matter does
ppear to have a uniform composition in all woods. It is,
er, always characterized by being soluble in alkaline liquids,
h it is insoluble in water. Sulphuric acid chars it, and an
us solution of chlorine attacks and dissolves it. When sub-
l to distillation in closed vessels, it evolves acetic acid; and
ound that the harder the wood, and the larger the proportion
is incrusting substance which it contains, the greater is the
rtion of acetic acid which is furnished when equal weights of
nt woods are subjected to destructive distillation. When
us fibre is heated with hydrate of potash an oxalate and
tate of the base are formed.

he ligneous matter is generally deposited in a state of mix-
ith a variable quantity of resinous matters, which colour
ood and increase its inflammability. The deposited fibre
ntains a certain proportion of saline matter; as well as small
ties of compounds containing nitrogen.

e applications of cellulin and of ligneous fibre in the arts
umerous and of great importance. Besides its every-day
the form of wood, the fibre constitutes the basis of all
cotton, and hempen goods ; and after these substances have
to be serviceable as textile fabrics, they are still, in the hands
paper-maker, convertible into a material scarcely less valuable.

58) *Paper-making.*—The rags which are employed in the
cture of paper are sorted, according to the material of
they consist, into linen, cotton, hempen, and woollen; and
erwards further separated into white, coloured, and black.
ams and knots are cut out, and the rags are then well
to get rid of dust and dirt. Coloured rags can be em-
in the preparation of writing-paper if they be first bleached
action of chlorine, which is often applied to them in the
s form. For this purpose the rags are moistened, and
on perforated shelves in wooden or stone chambers, into
the gas is transmitted. An excess of chlorine must be
lly avoided, because it is liable to enter into chemical com-
n with the fibre, and, by displacing a portion of the hydro-
to form a substitution compound, which, being destitute of
ty, furnishes a brittle paper. Frequently, however, the rags,
ing been reduced to the form of *pulp*, are bleached by

means of chloride of lime. In all cases it is necessary to ensure the removal of the last traces of chlorine, which would not only cause the paper to become brittle, but when the paper is used for manuscript purposes would gradually discharge the ink. The removal of the chlorine is effected by the addition of a small quantity of sulphite or of hyposulphite of soda; if the sulphite be used the chlorine is converted into chloride of sodium, and the sulphite into sulphate of soda, whilst sulphurous acid is se free:—

$$2(2\,NaO,S_2O_4)+Cl_2=2\,NaCl+2\,NaO,S_2O_6+S_2O_4.$$

The rags having been partially cleansed, either in their bleached or unbleached condition, are reduced by mechanical means into fibrous paste, or smooth uniform pulp, with water. This pulp then extended over wire strainers in a layer of uniform thicknes which when drained forms a film of paper. If this be simpl dried and pressed it forms *blotting,* or *filtering* paper, and is t porous to be used as writing-paper. In order to fit it for the in it is *sized,* or coated with a mixture of weak fine glue and alum by which means it is rendered less permeable to water. Man manufacturers mix the size with the pulp before it is made int sheets, but in this case it is necessary to employ a size of a d scription different from that which is applied to the finished sheet The size which is to be mixed with the pulp usually consists of mixture of three parts of a resinous soap and two parts of starc to which a small quantity of alum is added.

Of all the numerous materials which have been tried as th basis of paper, none has been found so well adapted for the pu pose as linen rags. Straw has been used to some extent as material for paper, and it was at one time thought, owing to th abundance and cheapness of this substance, that it might be ma a valuable substitute for rags, the supply of which is becomin inadequate to meet the demand; but the loss of material, from i brittle nature, during the process of manufacture, and other unfo seen circumstances, more than counterbalanced the advanta gained from the abundance of the supply.

(959) *General Remarks on Starch and Woody Fibre.*—T facts already mentioned show the ready convertibility of organized bodies, starch and lignin, into others which, though organic origin, are yet devoid of structure, and therefore of a l complicated nature. In most cases great similarity exists in ultimate constitution of these bodies, many having identically same composition as those from which they are derived; othe

entical, differ among each other only in the presence or of the elements of water. It is, therefore, not surprising adual transition should occur from the elaborate arrange- the dense and compact tissue of the wood into the com- loose texture and low organization of starch; the lig- sue undergoing modifications of density, which gradually from the compact structure of the *lignum vitæ* to the ells of the fungus, or lichen. The tissue of the Iceland example, presents a close analogy with starch; it is gra- integrated by boiling, it swells up to a gelatinous mass, is a magma colourable by iodine: thence we arrive at h, and gradually, as the organization of this body is by the successive action of chemical agents, the addition produces a coloration less and less intense, until in the rmation of dextrin it disappears altogether; and at length ugar, in place of the cellular structure, crystalline form apparent.

On the Decay of Woody Fibre, and the Means of Pre- .—When wood in a moist state is exposed to the air, it undergoes decomposition; a species of fermentation is d by the nitrogenized constituents, in consequence of ygen is absorbed, carbonic acid and water are exhaled, wood crumbles down into a blackish brown vegetable alled *humus, ulmin,* or *gein.* This decay occurs most n young spongy wood, since this admits the air more nd at the same time contains a proportionately larger of the albuminous substance than the harder and older

decomposition of this albuminous component favours the f lichens and fungi, and encourages the ravages of insects, the albuminous portions in particular afford the means nent. It is obviously a matter of high importance to he wood, as far as possible, from these influences. A l coating of some substance impervious to air and mois- ers this object in great measure, so long as it can be d entire. Such a coating is usually supplied by the n of layers of resinous or oily matter, which, if needful, hickened with metallic oxides; as in the ordinary pro- tarring and painting. But a more effectual method of on consists in steeping the wood, sail-cloth, cordage, or lar materials, for a given time in crude coal-tar kreasote. aline solutions have been *employed,* but they have been gradually abandoned. Kyan made use of a solution of corrosive sublimate, containing $\frac{1}{60}$th to $\frac{1}{70}$th of its weight of the mercurial salt. Boucherie employed a solution which usually contained about 1 per cent of raw acetate of iron, or of sulphate of copper.

Products of the Decay of Woody Fibre.—When vegetable mould, or mouldered wood from the trunk of a decaying tree, is digested in a weak solution of potash or of soda, a brown liquid is formed, from which, on the addition of an acid, a blackish brown precipitate is obtained. This precipitate is readily soluble in alkalies, and always retains a considerable proportion of nitrogen. It is regarded by Mulder as a mixture of three substances, none of which is crystallizable, but which he considers as compounds of water, or of water and ammonia, with three different acids, viz., 1. *Geic acid*, $C_{40}H_{12}O_{14}$; 2. *Humic acid*, $C_{40}H_{12}O_{12}$; and 3. *Ulmic acid*, $C_{40}H_{14}O_{12}$. These substances are obviously the product of vegetable matter in stages of decay more or less advanced. Mulder found the brown substances formed by the prolonged action of dilute acids at a boiling temperature upon sugar, to resemble the ulmic and humic acids from mould, both in composition and in properties. Besides these acids, Berzelius has pointed out the existence of two other allied bodies, which have received the name of crenic and apocrenic acids (from κρήνη, a spring); they have been found in many mineral waters, and accumulate in the ochry deposits that occur around the margin of ferruginous springs. *Crenic acid* ($3HO,C_{24}H_{12}O_{16}$, Mulder) has also been found associated with ammonia, in vegetable mould. It forms a yellow solution, which retains ammonia with obstinacy, and rapidly absorbs oxygen, becoming converted into *Apocrenic acid* ($2HO,C_{48}H_{11}O$ Mulder); the latter acid furnishes a brown solution in water, and also retains ammonia strongly. Indeed, this property of retaining ammonia with obstinacy is a characteristic of those imperfectly defined acid products which are formed during the decay of ligneous matter, and it is connected in an important manner with the functions which they subserve in supplying nutriment to growing vegetables, towards the support of which they contribute largely.

By the decay of herbaceous and aquatic plants in marshy s a material somewhat similar to humus is formed, which accu lates in beds often of great depth and extent, constituting bogs. In Holland the peat is often 6 feet thick, and in the g central bogs in Ireland it even extends to a depth of 30 o feet. Dried peat is found upon analysis to yield a larger pro tion of carbon than woody fibre; it likewise contains an excess of hydrogen over the oxygen.

The process of decay in ligneous tissue is liable to considerable variation, according as it is allowed to take place with free access of air, or is effected under water with but a scanty supply of oxygen from without. When the atmosphere has free access, De Saussure found that the oxygen of the air is converted into an equal volume of carbonic acid, while at the same time a large quantity of water is evolved. According to Hermann, a small proportion of nitrogen is absorbed during the process, and ammonia is generated. The water produced is at the expense of the oxygen and hydrogen contained in the ligneous tissue, so that the mouldered product contains a larger proportion of carbon than the wood upon which the experiment was conducted.

If the moistened wood be excluded from air, a small quantity of carbonic acid is evolved during its decay, accompanied, as in the former case, with the separation of water; and under certain circumstances marsh gas (C_2H_4) is liberated in considerable abundance. (See also p. 126.)

Coal and other Combustible Minerals.

(961) The foregoing facts connected with the gradual decay of woody fibre and vegetable tissue, have a special interest, not only in their bearing upon the value of vegetable matter as a manure, but also in reference to the origin of the enormous masses of fossil fuel which are stored up in the bowels of the earth, and which are the result of complicated chemical changes under variable circumstances of temperature, moisture, and pressure—acting either upon plants which grew upon the spot, as in peat bogs now in process of formation, or upon the débris of trees or plants drifted from a distance, and accumulated in particular localities, as is now occurring in the deltas of the Mississippi, and other large rivers.*

The deposits of fossil combustible matter may be subdivided

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* Most of the bituminous coal appears to have been formed from a cryptogamic vegetation, of which upwards of 500 species have been identified, including the ferns; *lepidodendra*, *calamites*, and *sigillariæ* are also abundant. The latter are especially interesting, as their roots, formerly mistaken for a distinct species of plant and termed *stigmaria*, are found in nearly every bed of clay immediately in contact with the coal, and the sigillaria have been found growing from them. This observation is one of high importance, as it proves that in most cases the plants actually grew upon the spot in which the coal is now found. In many instances the trunks of the sigillaria are found *in situ* traversing the seams of coal; the bark has in these cases been found converted into true pure coal, while the body of the tree appears to have decayed, and its internal cavity has been filled up with sandstone.

[illegible] 2. Fossil resins, and bitumen ; 3. Lignites, or brow [illegible] 4. [illegible], or caking coal ; 5. Steam coal ; and 6. An- [illegible]

[illegible] Peat.—The vegetable origin of this substance is at onc [illegible] inspection. Peat is formed only in the temper [illegible] the globe ; in tropical climates the decay of vegetab [illegible] with too much rapidity to allow of the accumul [illegible] when the decomposition takes place slow [illegible] growth is comparatively rapid. Peat diffe [illegible] and density ; that taken near the surface [illegible] reddish brown colour, very porous, and preserv [illegible] of the plants. When dry its density o [illegible] that from the deeper layers is much dens [illegible] becomes much darker coloured as the depth [illegible] often exhibits little or no traces of its veget [illegible] The proportion of earthy matter is greater in the dens [illegible] the deeper parts of the bog. In surface-p [illegible] exceed 1 or 2 per cent. ; whilst in the dee [illegible] per cent. is a common proportion, and at t [illegible] bog it sometimes amounts to 30 per cent. upon t [illegible] Freshly cut peat often contains 40 or 50 p [illegible] and the peat sold in Dublin, after being dried [illegible] for many months, still retains from 15 to 25 p [illegible] In Bavaria, peat is dried extensively for use in t [illegible] and at Königsbrunn it has been for seve [illegible] the puddling furnaces in the conversion of c [illegible]

[illegible] Resins, and *Bitumen*.—These substances inclu [illegible] *asphalt*, *retinite*, and many other allied bodi [illegible] contained in the tertiary strata. In many i [illegible] products of the action of an elevated temp [illegible] vegetable bodies ; and when this is the case, th [illegible] deposits which impregnate the strata around : und [illegible] masses of igneous rock, such as basalt or tr [illegible] their immediate neighbourhood. In oth [illegible] occur in regular beds, which appear to ha [illegible] manner similar to the deposits of true co [illegible] contain the bitumens and resins disse [illegible] small quantities. They are more or l [illegible] and the essential oils. Although c [illegible] consumed as fuel. Asphalt is largely u [illegible] an artificial paving material, and the fi [illegible]

s are employed in the formation of a species of black varnish
namel for leather.

3. *Lignite, or Brown Coal.*—This species of coal generally re-
its woody lamellar structure to a considerable extent, though
is respect there are great differences; as its name implies, it
a brown colour. When first raised it contains a large pro-
ion of moisture, amounting sometimes to 40 per cent., 15 or
er cent. of which is retained after exposure to the air for
r months. When distilled in closed vessels it yields a coke
h does not cake together, and in which the original form of
fragments is preserved; the ash is less abundant than in peat.
true lignites occur in the tertiary strata.

4. *Bituminous or Caking Coal.*—This is the most highly prized
ty of coal, and is the most abundant product of the British
fields. It occurs above the old red and beneath the new red
stone, in what geologists have termed from its presence *the*
measures. There are several varieties of bituminous coal:
, as those of the Scotch *parrot coal*, are of a brownish black
r, and a slaty structure; when heated in closed vessels they
a large quantity of gaseous matter, and leave a coke which
t incompletely fused and coherent. The Lancashire *cannel*
is another form, which is characterized by its conchoidal
ure, and the waxy lustre which it exhibits. It is hard, and like
is often cut and polished for ornamental purposes: it is of a
brownish black colour, yields a good deal of gas, and leaves an
fectly fused hard lustrous coke; both these coals are highly
as *gas coals*. *Newcastle coal* represents a third variety; it is of
blue black colour; has a brilliant lustre, and a cubic fracture;
rns with a bright luminous flame, and is much valued as
hold fuel; it furnishes a coke which is much swollen, caked
ler, and possessed of a high lustre.*

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* A remarkable bituminiferous deposit occurs amongst the coal measures in
ighbourhood of Bathgate near Edinburgh, which has been sold under
of 'Boghead Cannel Coal,' and has been extensively employed to
inferior descriptions of coal in the manufacture of coal gas. It con-
m 18 to 25 per cent. of an aluminous ash, which retains the form of
ral when it is burned in the open fire; when distilled at a low tem-
e in closed vessels, the mineral gives off a very large proportion of
hydrocarbons mixed with a certain quantity of dense gaseous hydro-
The mass left after distillation is remarkable for the small propor-
carbon (from 6 to 10 per cent.), which is left behind in the ash. A
r lawsuit arose upon the question whether or not this substance was to
rded as a *coal*. The term coal, however, being one rather of popular
scientific language, and not admitting of accurate definition, the
of the chemists, geologists, and histologists who were examined upon
were divided, and the case *was decided upon* a collateral issue.

5. *Steam Coal.*—This is a coal intermediate in quality between the bituminous coals and the anthracites; it burns freely and with flame, giving out a steady heat, but it does not yield sufficient volatile matter to be advantageously employed in the preparation of coal gas. It is well fitted for use in the steam navy, since it does not crumble readily in the hold of a vessel during its rolling, and it emits but little smoke. It furnishes a coke which scarcely cakes together, and which possesses but little coherence or lustre. Much of the Welsh coal is of this description.

6. *Anthracite.*—The *stone coal,* or *culm,* as this variety is sometimes called, is found in the lowest portion of the carboniferous strata. It contains but a small portion of volatile matter, and burns almost without flame with a steady red glow. When heated it splinters into small fragments, a circumstance which often occasions considerable inconvenience in its application as fuel. The most compact forms burn indeed with great difficulty. This coal is black; it has a high lustre, and often exhibits an iridescent play of colours; its fracture is lamellated parallel to the bed from which it was taken, but the cross fracture is oblique or conchoidal. The coke obtained from it differs little in appearance from the original coal either in bulk or in weight. Anthracite is extremely abundant over vast tracts of North America, but much of it is so compact that it is scarcely applicable as a fuel. A large quantity of excellent anthracite is obtained from the South Wales coal field.

The subjoined tables will give an idea of the composition of wood, and will illustrate the progress of its decay. They also furnish a synoptic view of the composition of some of the principal varieties of coal, in the order of their occurrence in successive geological stages. The proportion of oxygen, it will be seen, diminishes rapidly, and that of the hydrogen more slowly, as the coal passes from lignite towards anthracite, in which form it consists of nearly pure carbon.

Observation has proved that during these changes oxygen in small quantity is absorbed whilst carbonic acid and carburetted hydrogen are evolved in large quantities. It may be worth while to point out the simple mode in which we may from these facts theoretically explain the conversion of wood into coal under the influence of a very limited supply of oxygen, whilst the vegetable matter is submerged in water at a moderate temperature. If we assign to wood the empirical formula $C_{34}H_{24}O_{22}$ founded upon the analysis of oak given in the table which follows, the approximative empirical formulæ for peat will be $C_{20}H_{11}O_8$; for Bovey lignite, $C_{27}H_{14}O_7$; for Wigan Cannel, $C_{26}H_{10}O_2$; and for the Welsh

$C_{40}H_8O$. Now, if a small amount of oxygen, such as ipplied by solution in water, be supposed to act upon issue, each of these varieties of fuel might be formed ration of marsh gas, carbonic acid, and water, in the oportions :—

$$\overbrace{H_{24}O_{22}}^{\text{ood.}}+6\,O_4=8\,\overbrace{C_{20}H_{11}O_8}^{\text{Peat.}}+24\,\overbrace{C_2H_4}^{\text{Marsh Gas.}}+32\,\overbrace{C_2O_4}^{\text{Carb. Acid.}}+4\,\overbrace{H_2O_2}^{\text{Water.}}$$

$$\overbrace{H_{24}O_{22}}^{\text{ood.}}+2\,O_4=8\,\overbrace{C_{27}H_{14}O_7}^{\text{Lignite.}}+8\,C_2H_4+20\,C_2O_4+24\,H_2O_2$$

$$\overbrace{H_{24}O_{22}}+4\,O_4=8\,\overbrace{C_{26}H_{10}O_2}^{\text{Cannel.}}+8\,C_2H_4+24\,C_2O_4+40\,H_2O_2$$

$$\overbrace{H_{24}O_{22}}+5\,O_4=4\,\overbrace{C_{40}H_8O}^{\text{Anthracite.}}+24\,C_2H_4+32\,C_2O_4+32\,H_2O_2$$

ount of ash left by different kinds of coal is very variable. species of coals the fixed ash appears to be disseminated ly through the mass, but in the coarser varieties, thin on pyrites, and at other times, as in the Newport coal, laminæ composed of the mixed carbonates of lime, nd protoxide of iron are found. It is obvious that seams occur, their components must have been carried ss by infiltration. The ash of pure coal furnishes but ntities of the salts of the alkalies; it usually contains ne or magnesia, the bulk of it consisting of silicate of th variable amounts of oxide of iron. Vaux also found pper and lead in most of the coals which he analysed.

Composition of Wood and Coal.

, d. M.	Oak, Decayed Liebig.	Humus from Decayed Oak. Meyer	Humus from Decayed Oak. Will.	Peat. Dartmoor. Vaux.	Peat. Vulcaire Regnault.	Asphalt. Mexico. Regnault.	Lignite. Bovey. Vaux.	Lignite. Dax. Regnault.	Boghead. W.A.M.
				0·849		1·063	1·129	1·272	1·196
				29·30		9·0	30·8	49·1	30·23
	53·47	54·0	56·0	54·02	56·25	78·10	66·31	69·52	63·10
	5·16	5·1	4·9	5·21	5·63	9·30	5·62	5·59	8·91
				2·30	} 32·54		0·56	} 19·90	} 7·25
	41·37	40·9	39·1	38·17		9·80	22·86		
				0·56			2·36		0·96
				9·73	5·58	2·80	2·27	4·99	19·78
				The same, ash free.					
				59·73	59·57	80·34	67·85	73·18	78·67
				5·91	5·96	9·57	5·76	5·88	11·11
				2·54	2·09	} 10·09	0·58	} 20·94	
				31·82	32·38		23·39		10·22
O_{22}				$C_{20}H_{11}O_8$			$C_{27}H_{14}O_7$		$C_{22}H_{19}O$

Composition of different Varieties of Coal—(Continued.)

Variety	Parrot.	Cannel.	Caking.	Dry.	Dry.	Steam.	Anthrac
Locality	Lesmahagow.	Wigan.	Newcastle.	Wolverhampton	St. Helen's.	Newport.	S. Wales.
Authority	W. A. M.	Vaux.	Richardson.	Vaux.	Vaux.	W. A. M.	Vaux.
Specific gravity	[illegible]	1·276	1·280	1·278	1·279	1·309	1·392
Coke	45·3	60·36		57·21	65·5	75·1	92·1
Carbon	[illegible]	80·07	86·75	78·57	75·80	81·47	90·39
Hydrogen	[illegible]	5·53	5·24	5·29	5·22	4·97	3·28
Nitrogen	[illegible]	2·12	6·61	1·84	1·92	1·63	0·83
Oxygen		8·08		12·88	10·99	5·32	2·98
Sulphur	[illegible]	1·50		0·39	0·90	1·10	0·91
Ash	[illegible]	2·70	1·40	1·03	5·17	5·51	1·61

The same, ash free.

Carbon	78·26	82·29	87·95	79·38	79·93	86·27	91·87
Hydrogen	8·21	5·68	5·32	5·34	5·50	5·26	3·33
Nitrogen	13·53	2·18	6·72	1·86	2·03	1·73	0·84
Oxygen		9·32		13·02	11·58	5·54	3·01
Empirical formula	[illegible]	[illegible]	[illegible]				$C_{40}H_{9}O$

§ V. On Fermentation.

(962) Under the term fermentation, frequent mention has b made of a particular change which saccharine bodies underg consequence of which they become converted into carbonic a and alcohol. Many other substances, however, besides sugar, a susceptible of an analogous change, and the term *fermentatio* now applied to various transformations which organic compou experience under the influence of a small quantity of organ matter, which is itself in a state of active alteration. This act substance, which is termed a *ferment*, neither imparts anything nor receives anything from, the substance which is undergo fermentation. During this change, the body which is experiencing fermentation is gradually broken up into two or m substances of simpler composition; in certain cases the elem of water are assimilated, in others they are separated, whilst i third class of decompositions water is neither separated nor assimilated.

For example, when fruit sugar is placed in contact with [illegible] yeast, the sugar is simply converted into carbonic acid alcohol, the yeast acting as the ferment;—

$$\underbrace{C_{12}H_{12}O_{12}}_{\text{Fruit sugar.}} \text{ gives } \underbrace{2\,C_2O_4}_{\text{Carb. acid.}} + \underbrace{2\,C_4H_6O_2}_{\text{Alcohol.}}$$

No assimilation or separation of water occurs in this case.

when grape sugar, $C_{12}H_{14}O_{14}$, is subjected to fermentation, carbonic acid and alcohol are formed as before, and the elements of water are eliminated:—

$$C_{12}H_{14}O_{14} = 2\ C_2O_4 + 2\ C_4H_6O_2 + H_2O_2.$$

Again, when cane sugar is submitted to fermentation, it assimilates the elements of water, first becoming changed into fruit sugar, and this substance is afterwards broken up into carbonic acid and alcohol as before;

$$2\ C_{12}H_{11}O_{11} + H_2O_2 = 2\ C_{12}H_{12}O_{12}; \text{ and } C_{12}H_{12}O_{12} = 2\ C_2O_4 + 2\ C_4H_6O_2.$$

The different varieties of fermentation receive their distinctive name from the principal products which they furnish: for example, when spirit of wine is formed from sugar, the change is called the *alcoholic* or *vinous* fermentation; when lactic acid is converted into butyric acid, the process is termed the *butyric* fermentation, &c.

In all cases of fermentation the following conditions are essential:—1, the presence of water; 2, a temperature ranging between the extremes of 40° and 110°; 3, a peculiar ferment (the nature of which varies in the different cases); 4, exposure for a longer or shorter period to the air; and 5, the body which is to undergo fermentation. It may be remarked, that in most instances the compounds susceptible of fermentation are crystallizable products. It is especially to be observed, although the ferment does not contribute any of its components to the results of fermentation, yet that it is itself destroyed during the operation; the products of its decomposition being generally discernible mixed with the results of the fermentation. This fact has an important bearing upon the theory of the process, but its significance will be best understood by tracing the operation through its different stages in the formation of alcohol.

(*a*) *Alcoholic Fermentation.*

(963) When the juices of plants or of fruits containing sugar, such for instance as *must* (the juice of the grape), are kept at a temperature of about 70° for some hours, a change begins to show itself. The liquid becomes turbid, and small bubbles rise to the surface; or in popular language, it begins to *work* or to ferment. This change is due in the first instance to the alterations produced in the albuminous and azotised matters, which all such juices contain, under the combined influence of atmospheric oxygen, warmth, and moisture. This azotised matter is decomposed, and an intes-

tine change commences, which after it has once begun, continues in vessels from which the further access of air is prevented. As the fermentation proceeds, a continual disengagement of heat is maintained, whilst a constant extrication of gas continues; this gas, if collected, is found to consist entirely of carbonic acid. After a time the escape of gas diminishes, and at length ceases; if the liquid be now examined, the sweet taste of the sugar will have disappeared, and the solution will have acquired a flavour more or less spirituous. If this liquid be distilled, the first portions that come over will be found to contain an inflammable product lighter than water, which is easily recognised as dilute spirit of wine or alcohol.

(964) *Properties of Yeast.*—Upon examining the liquid which remains after fermentation is complete, it is found to contain a multitude of small oval organized bodies which do not exceed $\frac{1}{250}$th of an inch in diameter, and which when viewed under the microscope, are seen to consist of nucleated cells presenting the appearance shown in fig. 359, page 132. These cells form the essential constituent of *yeast*, which is obtained in great abundance during the fermentation of wort in the manufacture of beer.

Beer yeast is the substance which possesses, in the highest degree, the power of producing the alcoholic fermentation. Its efficacy in this respect is easily proved by the following experiment:—Dissolve 4 parts of pure cane sugar in 20 parts of water, and add 1 part of fresh yeast; then expose the mixture to a temperature of about 80° F. In less than an hour fermentation will commence, and carbonic acid will be evolved in abundance.

Yeast, when in its active condition, always exhibits a slightly acid reaction; if thoroughly washed, the globules are much less active, but they again acquire activity by exposure for a few hours to the air, during which time the acidity is again developed. The addition of a minute quantity of some of the vegetable acids, such as the acetic or the tartaric acid, to washed yeast, immediately restores its activity, but if a larger quantity of the acid be employed the process of fermentation is arrested. The strong mineral acids, particularly the sulphuric acid, when present even in small quantity, immediately put a stop to the alcoholic fermentation; the same effect is also produced by solutions containing traces of sulphurous acid. It is also checked by the addition of a small quantity of free alkali. Many other circumstances likewise put an immediate stop to the process of fermentation. For example:—A solution which contains more than one-fourth of its weight of sugar, cannot be made to ferment; the presence of 20 per cent. of alcohol or upwards, also puts an end to the process; the addition of a strong solution of common salt, or the presence of many metallic salts in the liquid, such for instance as nitrate of silver, corrosive sublimate, and sulphate or acetate of copper, check it immediately. The occurrence of fermentation is also prevented by the presence of small quantities either of oxide of manganese, or of oxide of mercury, of strychnia, or of quinia. Small quantities of kreasote, of oil of turpentine, and of many other essential oils, have a similar effect. If, however, fermentation has once commenced, the vegetable bases have no specific power of arresting the process.

On the other hand, neither solution of arsenious acid, of acetate of lead, nor of tartar emetic exert any retarding effect upon the progress of fermentation. If yeast be boiled for a few minutes, it is deprived of its power of exciting vinous fermentation. Such yeast, however, effects the conversion of sugar into mucilage and mannite. Yeast may be dried at a low temperature or by pressure, and preserved in this condition without losing its activity.

The part which the globules of yeast perform in exciting fermentation is extremely obscure. These globules appear to be fungi, or plants of a very low degree of organization, and as such, their particles are continually undergoing change. The following experiment of Mitscherlich appears to show that the sugar ferments only in those points which are in actual contact with the globules:—Over one extremity of a wide tube open at both ends a piece of filtering paper is tied, and this covered extremity is plunged into a weak solution of pure cane sugar; the liquid quickly penetrates the paper and rises in the tube, which may be supported so as not to touch the bottom of the jar of syrup; if a small quantity of yeast be now introduced into the tube, and the whole be set aside in a warm place, fermentation will be found to commence in an hour or two; but it will be confined to the portion of liquid within the tube;—that is, to those portions of syrup which are actually in contact with the yeast globules. The bibulous paper allows free communication between the liquid within and without the tube, but it prevents the globules from passing into the mass of syrup in the outer vessel.*

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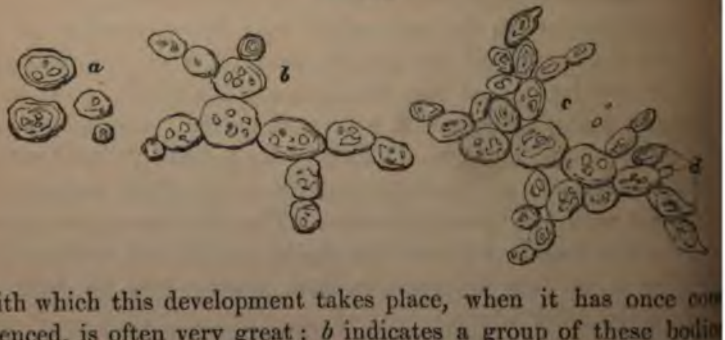
* Berthelot indeed states that it is possible to effect the alcoholic fermentation without the presence of yeast globules, by exposing a solution of glucose or of cane sugar, mixed with gelatin and chalk, to a steady temperature of about 100°, in vessels from which air is excluded. The solutions must be saturated with carbonic acid, and the experiments conducted over mercury. But the presence of yeast globules is by *no means necessarily* excluded under

Varieties of Yeast.—According to the observations of Mitscherlich, who has carefully watched the development of the yeast plant under the microscope, there are two modifications of yeast, viz., *oberhefe* (surface yeast), and *unterhefe* (sediment yeast); these two varieties are propagated in different ways, and each produces specific results upon the fermenting liquid.

The *unterhefe* is the ferment of the Bavarian beer, which i allowed to ferment very slowly and at a low temperature; the formation of acid bodies, such as the lactic and acetic acids, is thus avoided, and the beer is more highly esteemed from their absence. The *unterhefe* consists of isolated globules of very varying dimensions. It appears to be propagated by spores thrown out from the larger cells, and not by buds and offshoots as is the case with the surface yeast; the temperature must not be allowed to rise beyond 45° nor to fall below 32° F.

Surface yeast is developed rapidly at a temperature varying from about 70° to 80°, and is the more active of the two forms in producing the alcoholic fermentation. The development of the yeast globules may readily be watched under the microscope, by placing a drop of some saccharine infusion, such as wort, between two plates of glass, with a minute quantity of yeast. The granules will at first exhibit the appearance shown at *a*, fig. 359, where they can be seen to possess an outer cell wall, within which is a quantity of granular matter. In the course of a few hours some o these cells throw out buds such as are shown at *d*. The rapidit with which this development takes place, when it has once commenced, is often very great; *b* indicates a group of these bodi probably all developed from the large central cell; *c d* shows th same group three hours later: within nine hours after it w

FIG. 359.



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these circumstances, and the researches of Schröder as well as of Pasteur (p. 134) seem to show conclusively that no alcoholic fermentation occurs w due care is taken to exclude the spores of the yeast fungus.

irst observed an oval patch of cellules had been formed, containing between seventy and eighty separate cells, in which the original cell was distinctly visible in the centre, and around it were grouped the new cells, decreasing in size towards the circumference; each of these cells contained the granular matter above spoken of, and fresh buds continued to form upon the exterior margin of the outer cells. The yeast cells frequently assume a more elongated form, flattened at the sides, but they continue to be developed in the same manner; both varieties may often be seen side by side under the microscope at the same time. The walls of these cells consist of a thin membrane which has the same composition as cellulin (Mulder): and within this membrane is an azotised gelatinous mass which here and there exhibits a kind of granular nucleus. This granular matter is soluble in acetic acid, and may thus without difficulty be separated from the cell membrane in which it is contained; it may then be precipitated for examination, by neutralizing the solution with carbonate of ammonia. The contents of the granules may also be extracted by means of a weak solution of potash, and can be precipitated by neutralizing it with acetic acid. When thus obtained, the precipitate has the properties and composition of protein.

Everything that destroys the vitality of these organized bodies destroys their power of exciting fermentation: for this reason too high a temperature, such as that of 120° F., stops the operation, and a depression of temperature also temporarily arrests it, though it is stated that even after exposure to a cold of 10° F. the fermentation is renewed when the temperature is allowed to rise.

The globules of yeast do not increase in number in solutions of pure sugar: on the contrary, during the process of fermentation, the granules undergo a gradual disintegration, the new buds which are formed, being produced at the expense of the material furnished by the decay of others. For the decomposition of 100 parts of sugar, about one part of yeast, calculating it in its dry state, is required. If the proportion of sugar to the yeast exceed this, the excess of sugar remains unaltered in the liquid; and if the cells be examined after fermentation has ceased, many of them will be seen to be ruptured and destroyed; and a certain quantity of lactate and acetate of ammonia, and other ammoniacal salts, will be found in the solution.

But although the yeast globules do not increase in quantity in a solution containing pure sugar only, they become rapidly developed in all saccharine vegetable infusions during fermentation, and multiply at the expense of the azotised matters which are always present in these liquids, and which form an essential part of the nutriment of the yeast plant. Owing to this cause the quantity of yeast is increased to six or eight times its original amount during the fermentation of beer.

Mitscherlich gives the following as the composition of ordinary washed yeast; first, when in a condition to excite fermentation, and secondly, in the partially exhausted state, after fermentation had ceased: in both cases the ashes have been deducted:—

	Entire cells.	Spent yeast.
Carbon	47·0	47·6
Hydrogen	6·6	7·2
Nitrogen	10·0	5·0
Sulphur	0·6	
Oxygen	35·8	

In this experiment the nitrogen in the spent portion was reduced to one-half of its former amount. This spent yeast, however, still contained an excess of active granules; but if entirely exhausted, it would furnish scarcely any nitrogen on analysis.

The inorganic matter contained in yeast amounts to a considerable quantity, not less than about 7·5 per cent. of the dried yeast. It consists entirely of phosphates of potash, soda, lime, and magnesia (Mitscherlich).

Pasteur's experiments seem to render it probable that in all cases alcoholic fermentation is connected with the assimilation of the sugar by the yeast plant during the development of the yeast globules; even when the globules are mixed with a solution of pure sugar, he considers that during the whole process of fermentation a development of fresh globules is taking place at the expense of those which are undergoing decomposition. The following is one of his experiments:—A quantity of washed beer yeast was divided into two equal portions, one of these was placed in a solution of pure sugar; the other portion was boiled with water, the decoction was filtered, and the filtrate added to a similar portion of pure syrup. A minute quantity of fresh yeast was now added to the second portion. In the first case 5 parts of yeast effected the transformation of 12·9 of sugar in six days, and then became exhausted: in the second case the liquid became turbid, fresh yeast was formed (at the expense of the azotised solution derived from the yeast globules), and 10 parts of sugar underwent fermentation in nine days. It appeared therefore, that during the conversion of the soluble portion of yeast into organized globules, a quantity of sugar was decomposed nearly equal to that decomposed by an equivalent amount of yeast in its natural state. Pasteur considers that the essential condition of fermentation is the conversion of albuminoid matter into organized globules.

The following analyses by Graham, Hofmann, and Redwood, show that during fermentation the azotised matters in the liquid are reduced in quantity, whilst the yeast plants are becoming developed:—Pale malt wort, of sp. gr. 1·088, which contained about 21 per cent. of solid matter before fermentation, yielded 0·217 per cent. of nitrogen, which would correspond to 3·43 per cent. of albumen; after full fermentation and removal of the yeast, the nitrogen amounted only to 0·134 per cent.; this existed no doubt partly in the form of ammoniacal salts, but if all were calculated as albumen, it would amount only to 2·11 of that substance.

The composition of the contents of the granules of yeast has already been stated to bear a close relation to that of albumen. This circumstance may afford some clue to the remarkable fact that yeast is never furnished except by the decomposition of albuminous matters. Various bodies which contain nitrogen furnish it when they have once begun to decay. Thus white of egg, muscular tissue, and cheese, during decomposition in the presence of saccharine solutions produce these globules, and true fermentation begins.

Berthelot has shown that by employing an azotised substance such as the tissue of the pancreas, or, still better, a portion of casein obtained from poor cheese, and adding chalk to the liquid to prevent it from acquiring an acid reaction at any time, a number of substances not hitherto regarded as susceptible of the alcoholic fermentation, may be made to furnish alcohol and carbonic acid, whilst a portion of lactic or of butyric acid is formed. The temperature of 100° F. is that most favourable for obtaining these results, and a period of several weeks is often requisite. The maintenance of the liquid in a neutral state by means of chalk or some corresponding substance, is an essential condition. Not only do the ordinary sugars furnish a certain amount of alcohol when thus treated, but starch, sorbin, and gum give similar results. Even mannite, dulcite, and glycerin may thus be made to yield alcohol, hydrogen in these cases being developed at the same time. During the progress of these fermentations it was not possible in any case to detect the conversion of the gum, the starch, the dulcite, the sorbin, the mannite, or the glycerin into a fermentable variety of sugar as an intermediate step in the act of fermentation; this, however, was most probably because the sugar was decomposed as fast as it was formed. A small quantity ot gaseous nitrogen was commonly found amongst the products, and was traced to the decomposition of the azotised matter which occurs simultaneously with the metamorphosis of the saccharine body.

(965) *Progress of Fermentation.*—Much interesting information relative to the changes which solutions of sugar of various kinds undergo during fermentation may be obtained by examining them at intervals by means of a beam of polarized light. If a solution of starch sugar be mixed with yeast, the right-handed rotation which such sugar possesses in its natural state slowly diminishes, in a degree proportioned to the quantity of sugar which has undergone fermentation (Mitscherlich). But if a solution of *inverted* cane sugar (937) be watched in like manner from time to time, the phenomena are more complicated; the left-handed rotation undergoes no decrease until about three-fifths of the sugar has been decomposed, after which the rotatory power rapidly diminishes as the fermentation proceeds, but there is *no inversion* of the rotation. Dubrunfaut, who made these observations, remarks that this uncrystallizable sugar must consist of a mixture of at least two, and possibly of more modifications of sugar; one of which is neutral and is that which is first fermented, and the other is possessed of left-handed rotation, and does not undergo fermentation until the neutral sugar has all been decomposed.—(*Ann. de Chimie,* III. xxi. 172.)

It has been already mentioned that when cane sugar is subjected to the vinous fermentation, it undergoes a preliminary change in consequence of the necessity of assimilating the elements of water. Owing to this circumstance, a much larger quantity of yeast is required in order to produce the fermentation of sucrose or cane sugar than is needed by glucose. Berthelot states that the ferment by which this conversion of cane sugar is converted into glucose is contained in the soluble portion of ordinary yeast, and does not reside in the globules. It has been observed by Dubrunfaut, that if a solution of cane sugar which has been mixed with yeast be examined by polarized light before fermentation commences, the rotatory power upon polarized light will be inverted, and it will be found to have become left-handed, showing that the cane sugar has acquired the additional amount of water which it needed, and has thereby become altered into uncrystallizable sugar. The same change is also strikingly shown by the increase in density which a solution of cane sugar undergoes previous to entering into fermentation. This circumstance was pointed out by Graham, Hofmann, and Redwood, in their researches upon the decrease in density which saccharine solutions undergo during fermentation.

See their "Report upon Original Gravities," *Q. J. Chem. Soc.*, 232.)

It was ascertained by these chemists that when quantities of ne sugar, starch sugar, caramel, and dextrin, which contained qual quantities of carbon, were dissolved in water and diluted till solutions were equal in *weight*, the density of these solu- ons varied greatly, as will be evident on inspecting the following ble: from which it appears on comparing together quantities of different solutions, equal weights of which contain equal quanti- s of carbon, that starch sugar furnishes the densest solution; xt to this comes malt wort, which owes its sweetness to starch gar; then comes cane sugar; whilst dextrin gives a solution of aller specific gravity; and caramel a solution the least dense of of the substances compared together:—

Parts of Cane Sugar in 1000 of Solution.	Sp. gravity of Solution of				
	Starch Sugar.	Pale Malt Wort.	Cane Sugar.	Dextrin.	Caramel.
25	1·0104	1·0100	1·0101	1·0097	1·0087
50	1·0208	1·0203	1·0202	1·0193	1·0173
75	1·0313	1·0306	1·0302	1·0288	1·0262
100	1·0424	1·0412	1·0406	1·0383	1·0349
125	1·0535	1·0521	1·0510	1·0479	1·0438
150	1·0649	1·0630	1·0618	1·0573	1·0528
175	1·0760	1·0742	1·0729	1·0669	1·0623
200	1·0878	1·0855	1·0838	1·0776	1·0718
225	1·0994	1·0972	1·0952	1·0863	1·0813
250	1·1114	1·1090	1·1067	1·0958	1·0910

Suppose for instance that 175 grains of cane sugar were dissolved ter, and the solution diluted till it weighed 1000 grains; it have a sp. gr. of 1·0729. This solution if converted into sugar would become increased in specific gravity: so that tion of starch sugar which contained in 1000 grains of uid a quantity of this sugar which would be furnished by ount of cane sugar contained in the first solution, would as is represented in the second column, a specific gravity of

a direct experiment, made for the purpose of observing this it was found that a solution of cane sugar, to which a suf- quantity of yeast had been added to effect its fermentation, at first had a sp. gr. of 1·055, became in the course of of a sp. gr. of 1·058, though no fermentation had set in. other experiment, a solution of sp. gr. 1·055, containing its weight of yeast, increased *in specific* gravity in four days to a sp. gr. of 1·0579, although no appearance of f tion, or of other change, was manifest, loss by evaporati carefully prevented.

When sugar is fermented, it is assumed in theo wholly converted into carbonic acid and alcohol; but in this is never the case. It was found, by the chemists jus in three careful experiments on the fermentation of cane which 1½, 3, and 6 measures of yeast were respectively 100 measures of the syrup, that 4·4, 3·7, and 3·72 per cen sugar were converted into a brown soluble substance re caramel, and at the same time a little free lactic acid wa Pasteur (*Ann. de Chimie,* III. lviii. 323) finds succinic a produced, equal in quantity to not less than 0·5 per cen weight of the sugar employed. The same chemist also st glycerin is one of the usual products of the alcoholic ferment quantity sometimes amounting to 3 per cent. of the sugar e These are obviously secondary results, due, probably, to th passage of the ferment through different phases of de tion.

(*b*) *Fermentation of Bread.*

(966) *Composition of Bread Stuffs.*—The fermentatio takes place during the manufacture of bread is merely a tion of the alcoholic fermentation, produced by the actio yeast upon the saccharine matter, which is either naturall in the flour, or is developed by the action of the fe the starch. The chemical process of baking, however, rightly understood without a knowledge of the ordinary tion of the principal varieties of flour employed in the pr of bread.

When corn is ground in a mill, the grain is re powder, which may be separated by sifting into two portions—*flour* and *bran*. The bran is composed of the coloured outer covering of the grain, which is tougher a than the internal portions, and consequently is not re grinding to so fine a state of division: the flour is produc pulverization of the inner portion of the grain.

The most important constituents of the varieties of co food are—1. starch; 2. gluten, a peculiar substance allied to which confers the tenacity and toughness upon dough; proportion of sugar,* or of dextrin; 4. a little oily mat mall quantity of saline matter; and *6.* a skeleton of ligneous issue, which is the only portion of the seed not susceptible of digestion in the stomach. The proportions in which these ingredients are present in some of the principal varieties of grain used as food may be seen in the subjoined table. They vary, however, considerably in the same grain when grown in different climates. The proportion of gluten contained in wheat grown in the southern parts of Europe, and in the north of Africa, is considerably higher than in the best English-grown wheat; and the hard thin-skinned wheats furnish a larger proportion of gluten than the softer varieties of the grain.

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* Péligot considers that sugar does not exist ready formed in t in the freshly ground flour. He was unable to distinguish its pr

Components.	Whole Wheat Meal.			Maize.	Decorticated Rice.	Rye.	Peas.
	Polish.	Hardy White.	Algerian.				
	Péligot.			Boussingault.			
Water . . .	15·2	13·6	13·6	17·1	7·3	14·7	8·6
Starch . . .	61·3	60·8	59·8	59·0	83·0	65·1	56·9
Dextrin and Sugar. . .	6·3	10·5	6·4	1·5			
Azotised matter soluble	1·6	2·0	1·6	12·8	7·5	12·5	25·0
Azotised matter insol.	12·7	10·5	14·4				
Oily matter .	1·5	1·1	1·1	7·0	0·7	2·0	2·2
Fibre . . .		1·5	1·4	1·5	1·0	3·3	4·4
Salts . . .	1·4		1·7	1·1	0·5	2·4	3·1
	100·0	100·0	100·0	100·0	100·0	100·0	100·2

Components.	Bran of soft French Wheat.	Barley. Fresenius.	Hopetown Oats. Norton.
Water	13·9	13·90	12·80
Starch	51·0	48·06	56·89
Dextrin and		3·87	1·83
Sugar		3·75	3·93
Gluten or its equivalent	14·9	13·18	16·29
Oily matter	3·6	0·34	4·74
Fibre	9·7	13·34	1·03
Salts.	5·7	3·56	2·49
	98·8	100·00	100·00

The principal portion of the woody fibre is accumulated in the bran; but this substance likewise contains a large proportion of

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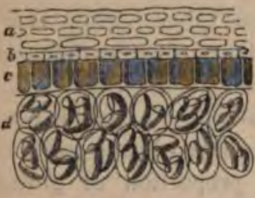
The aqueous solution of the flour was examined by optical means, and he did not find that lime was dissolved more freely by this solution than by pure water. If sugar were present, the lime should have been dissolved in proportion to the quantity of sugar in the liquid.

nutritive matter, for both gluten and oily matter are deposited in its cells more abundantly than in any other part of the grain; as may be seen by the result of its analysis, given in the preceding table. Fig. 360 shows a section of part of a grain of rye, highly magnified, *a* indicating the cells forming the outer coat of the seed; *b*, a single row of cells forming the inner seed coat; *c*, a layer of cells containing gluten, (these three together form the bran;) *d*, the white inner part of the seed filled with starch granules, lodged in the meshes of the cellular tissue.

Fig. 360.



Section of Grain of Rye. (After Johnston.)

(967) Gluten.—This characteristic ingredient in the cereal seeds may be obtained in a separate form by mechanical means. The flour is made into a paste or dough, with water, and placed in a bag of fine linen, in which it is kneaded in a gentle stream of water so long as the washings have a milky appearance: the starch is by this means removed in suspension in the water, and the sugar and the dextrin are dissolved. Upon the cloth is left a grey, sticky, tenacious, tasteless substance, resembling bird-lime in appearance, consisting mainly of gluten, mixed with small quantities of bran and starch, and traces of oily matter. When dry it forms a hard, brownish, horny-looking mass. The gluten obtained from wheat and from rye possesses a peculiar tenacity, which is not observed, to anything like the same extent, in that obtained from the other cereals; and it is this tenacity of the gluten which especially fits the flour of wheat and rye for conversion into bread. Gluten is soluble in cold acetic acid, and in weak solutions of potash or of soda. It may be precipitated unchanged from either of these solvents by neutralizing them exactly with an acid. The diluted mineral acids combine with gluten and form a compound which is insoluble in excess of the acid. Gluten in its moist state putrefies rapidly, ammonia is formed, whilst hydrogen and carbonic acid are evolved, and the mass acquires the smell of decaying cheese. Gluten, however, cannot be regarded as a single definite body; it consists of at least two distinct substances, one of which is soluble in hot alcohol, whilst the other remains undissolved when treated with this menstruum. This insoluble portion is regarded by Liebig and by Dumas as vegetable fibrin. As the alcoholic solution cools, it deposits flocculi, which have the composition and properties of casein. A third substance still remains in the alcoholic liquid, and gives to this solution a syrupy or gela-

nous consistence. On the addition of water, a white substance esembling albumen is precipitated; Dumas and Cahours have ermed it *glutin:* on treating it with ether a small quantity of t is extracted, and the glutin is left in a state of purity: it may e dissolved by strong hydrochloric acid, and communicates to it violet tint. It is, therefore, obvious that raw gluten contains everal azotised principles, which differ considerably in chemical roperties, though, as will be seen by the subjoined table, they are losely allied in ultimate composition:—

Constituents.	Dumas and Cahours.			Bence Jones.
	Gluten Fibrin.	Gluten Casein.	Glutin.	Crude Gluten.
Carbon	53·23	53·46	53·27	55·22
Hydrogen	7·01	7·13	7·17	7·42
Nitrogen	16·41	16·04	15·94	15·98
Oxygen and Sulphur .	23·35	23·37	23·62	21·38
	100·00	100·00	100·00	100·00

(968) *Preparation of Bread.*—In the preparation of bread, the flour generally requires the addition of about half its weight of water, but the proportion varies with the quality of the flour. It is the usual practice to mix a certain quantity of the flour with yeast, salt, and lukewarm water; after which it is thoroughly kneaded into a stiff paste, or dough, and put aside, at a temperature of about 70°, for an hour or two. The mass gradually swells up, or, as the baker terms it, the *sponge* rises; that is to say, the sugar in the dough is decomposed by the yeast; carbonic acid is set free at all points of the mixture, and, being imprisoned by the tenacious nature of the dough, the gas causes it to swell and become porous. When the sponge is in active fermentation it is thoroughly kneaded with the remainder of the flour, water, and salt, and set aside for a few hours. It is then kneaded a second time and cut into pieces of suitable size, after which it is put into an oven heated to a point between 450° and 550°; the heat causes the imprisoned air to expand still more, and gives the lightness of texture which characterizes good bread. During the process of baking, part of the water is expelled, 117 parts of dough, on the average, yielding 100 of bread; the granules of starch become converted into the pasty, or gelatinous condition: the temperature of the crumb never exceeds 212°, but the external surface of the loaf gradually becomes dry and hard, and losing a portion of its

chemically combined water, is partially converted into a substance allied to caramel (936), thus forming the *crust*. The bread is in this manner permanently fixed in the shape which it has acquired. During this baking, the alcohol formed by decomposition of the sugar, which corresponds in quantity to that of the carbonic acid, is expelled: some years ago a company was formed, in whose operations the collection of this spirit formed an important object. This end was attained by performing the baking in closed ovens, furnished with a still head for collecting and condensing the vapours. The project was, however, soon abandoned, and failed as a commercial speculation, owing in great measure to the dry unpalatable nature of the bread produced.

The French frequently employ *leaven* as a ferment instead of yeast. Leaven is dough kept from a previous batch for twenty-four hours in a warm place, till it has begun to undergo fermentation spontaneously. The decomposition which has commenced in the leaven spreads through the fresh mixture into which it is kneaded.

In England a species of unfermented bread has lately been manufactured to some extent; in this case also the sponginess is given to the dough by means of carbonic acid, but it is set free by the action of hydrochloric acid on carbonate of soda; common salt, a necessary ingredient in bread, being formed during the reaction, and a species of bread is obtained, which, as might be expected, is sweeter than ordinary bread, but not so light. A good bread of this description may, according to Pereira, be obtained by mixing the materials in the following proportions:—Wheat flour 7 lb., carbonate of soda 350 to 500 grains, water $2\frac{3}{4}$ pints, hydrochloric acid 420 to 560 grains. The soda and flour are first intimately mingled, and then made into dough with the mixture of acid and water. If the soda be not equally and thoroughly distributed, it is detected after the baking, by the formation of a yellow spot around any portions of it that have escaped neutralization. An ingenious method of preparing unfermented bread has recently been introduced by Dr. Dauglish. He forces gaseous carbonic acid, at a pressure of 100 lb. upon the square inch, into the water which is to be used in preparing the dough, and adds the aërated water to the flour and salt, effecting their intermixture by machinery, whilst the whole is retained under pressure in a strong closed iron receiver. The dough is then drawn off into pans or moulding baskets, and baked in the usual way. As soon as the pressure is removed, the dough rises from the expansion of the carbonic acid which has been thus intimately diffused through it.

Sponginess and lightness of texture are also sometimes given to pastry by the employment of sesquicarbonate of ammonia, which is mixed with the dough instead of yeast: on the application of heat, the salt is expelled in the gaseous state, and by its expansion mechanically produces the desired effect.

In the latter case it is not improbable that the alkaline nature of the salt has an important influence upon the quality of the paste. Liebig has observed that in certain cases the employment of lime water in the manufacture of bread may be resorted to with great advantage. In order to understand the effect thus produced, it must be remembered that the peculiar toughness and elastic quality possessed by the dough furnished from the flour of certain of the cerealia, is dependent upon the gluten which they contain. It has been observed, that when gluten is kept in a moist state, it undergoes a change in properties, in consequence of which it slowly loses its soft, elastic, insoluble condition, and becomes converted into a substance closely resembling diastase. In this state it acts, as Odling has shown, upon the starch of the flour, causing a considerable amount of it to pass into the form of dextrin and of sugar. Bread prepared from such flour is sticky, heavy, and sodden. The convertibility of good flour into dough, by the addition of water, depends upon the peculiar power which fresh gluten possesses of combining with water, and of forming with it a soft tenacious substance which does not yield its water to dry bodies placed in contact with it. Gluten, however, is a very hygroscopic substance, and when flour is kept exposed to the air for some time, it gradually absorbs moisture; in consequence of which the gluten slowly undergoes the peculiar change above mentioned. This change in the qualities of the gluten occurs more rapidly in rye flour than in wheat flour.

It has been ascertained by Liebig, that flour in which the gluten has undergone this partial change, may have its original qualities restored by the substitution of lime water for common water in the preparation of bread: 100 parts of flour are to be mixed with 26 or 27 parts of saturated lime water, and a sufficiency of ordinary water must be added to furnish dough of the proper consistence. A given weight of flour, when treated with lime water, was found to yield 5 or 6 per cent. more bread than when made in the ordinary way, and the bread so obtained is stated to be more palatable than common bread.

It is to be hoped that this simple method will supersede the employment of alum, which is commonly resorted to by English bakers, to whiten the bread and to improve the tenacity of the dough of inferior flour. Even sulphate of copper, a still more deleterious ingredient, which in minute quantity exerts a similar effect upon the dough, has been employed in Belgium and elsewhere, for improving the appearance and sponginess of the loaf. Odling attributes the action both of lime water and of alum in improving the whiteness of bread to the power of preventing the transforming influence of the altered gluten upon the starch. The brown colour of so-called 'brown' and 'seconds' bread has been shown not to be due, as is frequently supposed, to the presence of bran; for flour from which all the bran has been carefully removed will yield a brown bread if mixed with an infusion of malt, instead of with water. The change of colour appears, therefore, to be due to the partial conversion of starch into dextrin during the fermentation, and not to the presence of the colouring matter contained in the bran, which, indeed, is rather of an orange than a brown colour.*

New and Stale Bread.—Newly baked bread exhibits a well-known elastic appearance, and possesses a certain degree of moisture, which renders it more palatable to most persons than bread which has been kept for a day or two, and has become firmer and drier in appearance, and which is commonly said to have become *stale*. It is very generally supposed that this change in properties in bread which has been kept for a few days, is owing to the loss of water by keeping. This, however, is not the case. The crumb of newly baked bread when cold, contains about 45 per cent. of water, and that of stale bread contains almost exactly the same proportion. The difference in properties between the two depends simply upon difference in molecular arrangement. Boussingault found that a loaf which had been kept for six days, though it had become very stale, had not lost more than 1 per cent. of its weight when new. This same loaf was then placed in the oven for an hour, and at the end of that time it had acquired all the properties and appearance of new bread, although during the second baking it lost 3½ per cent. of water. In another experiment a portion of bread was enclosed in a tight case, to prevent loss of water by evaporation, and allowed to become stale, then heated, and was restored to the condition of new bread; these effects were produced alternately, many times in succession, upon the same piece of bread: a heat of about 130° was found to be sufficient to reconvert stale into new bread. Every person who has seen a f stale bread toasted, may have satisfied himself that as during this operation been converted into the same that of new bread.

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* An interesting report by Chevreul, upon the investigations of Mège Mouriès, and upon a new method of bread-making which he has founded upon them, will be found in the *Comptes Rendus* for January, 1857.

(*c*) *Lactic Fermentation.*

t has already been mentioned, that sugar of milk ndergo the vinous fermentation under ordinary cir- . Milk, if it be kept in a warm temperature, may, ding, be converted into a spirituous liquor, which is use among the Tartars, who prepare it, under the *umiss*, from mares' milk. More commonly, however, lk, when allowed to ferment, yields a product of a very ture; *lactic* acid being formed, as may be seen in the se of milk turning sour in warm weather. This acid, ated form ($HO,C_6H_5O_5$), has the same ultimate com- sugar of milk; its oxygen and hydrogen being in the to form water: but the arrangement of its particles is icated than that of sugar of milk; and its formation good instance of the reduction of a complex body into mpler constitution, by the process of fermentation. In he casein or curd of the milk which is the basis of eese, acts as the ferment. Casein is rendered insoluble ence of acids, and therefore it becomes separated in the oluble flocculi, as soon as the milk turns sour. When d has been thus rendered insoluble, the conversion of o acid takes place very slowly, but if the acid be by carbonate of soda, or by chalk, the curd is redis- the fermentation or transformation is renewed in its ur. No extrication of gas nor absorption of oxygen ing the process; the only perceptible change being the appearance of sugar of milk and the production of this id, attended with the evolution of a peculiar offensive ng from the decay of the casein which accompanies the tion. According to the observations of Boutron and er animal matters undergoing decomposition are like- le of effecting the same transformation; moistened er exposure to the air for a certain time, and muscular inous tissues, at a particular stage of their decomposi- s the same property. But when the decomposition of tissue has advanced beyond this particular stage, dif- ucts are obtained: fermentations or transformations it is true, but the results of these changes are quite different, inasmuch as actions of a nature different from those required for producing lactic acid, are taking place in the body operating as a ferment. Not only sugar of milk, but starch, dextrin, cane sugar, and gum pass readily into lactic acid under the influence of casein and the other ferments already mentioned.

This subject will be further examined under the head of lactic acid (1138).

(*d*) *Viscous Fermentation.*

(970) Under certain circumstances, sugar becomes transformed into a mucilaginous substance, unattended by any evolution of gas; the liquid loses its sweet taste, and acquires a *ropy* consistence, as is sometimes observed when sweet wines are kept for a time. This mucilaginous substance is insoluble in alcohol, and yields a precipitate with subacetate of lead, but it differs from ordinary gum in not yielding mucic acid when oxidized by nitric acid. A solution of tannic acid produces a precipitate when added to such a liquid, and checks the progress of the fermentation. This circumstance explains the observation, that red wines which contain a good deal of astringent matter derived from the husk and stalks of the grape, are not liable to become ropy. The tendency of a sweet liquid to become ropy is also arrested by the presence of sulphurous acid or of alum in small quantities; the alum causes the precipitation of the ferment in an insoluble form.

It has been found that various substances, such as boiled yeast, or the water in which flour or rice has been steeped, speedily cause sugar to undergo this transformation; and the sweet juice of the beet root, owing to the presence of an analogous substance, if left in a warm place for a few days, spontaneously passes into the viscous state. A quantity of mannite is usually formed at the same time in these cases.

CHAPTER III.

THE ALCOHOLS AND ETHERS.

§ I. THE ALCOHOLS.

eneral Characters of the Alcohols.—The term alcohol ally applied specifically to the volatile inflammable liquor, which is the characteristic product of the fer- of sugar; but it has since been made generic, and is led to a class of bodies which possess chemical qualities to those of wine alcohol, and which are homologues of ance. Indeed, this class of compounds has already some striking illustrations of the existence of homo- ups (915).

rm alcohol, however, has received a still further exten- t is now applied to all neutral compounds of carbon, and oxygen, which unite directly with acids, water inated whilst ethers are produced. The ethers so ob- themselves neutral compounds of peculiar constitution. earches have indeed led to the discovery of several dis- ties of alcohols, including monobasic, dibasic, tribasic, sic groups. The monobasic alcohols are those which longest known, and they are the most numerous and rtant.

Groups Isologous with the Monobasic Alcohols and vatives.—The progress of research into the products composition of organic compounds, has disclosed the f a number of groups which bear a close relationship f the monobasic alcohols, already adverted to: this p, however, is not one of homology; for if the new ere homologous with those previously known, they nselves be members of the group to which these bodies

oups of which we are now speaking are *isologous* with s—that is to say, that the compounds which constitute se groups are related to each other in a manner similar he components of the alcohol group with which they are For example, a class of compounds is known to the composed with the assimilation of the elements of water into a fat acid, and into glycerin, a body which in this respect presents an analog with alcohol; but he did not see the precise difference, and the com pleteness of the parallel has only recently been established, and th distinction between the two pointed out. Berthelot, by synthe experiments (1069) has shown that the neutral fats are derived fr three atoms of a monobasic acid, and one atom of glycerin; glyce being in fact a *triatomic alcohol*, and presenting a constitution wh has its representative among the acids, in the tribasic phosphoric a

Stearin ($C_6H_5O_3$, 3 $C_{36}H_{35}O_3$), for instance, consists of

$$\overbrace{C_{114}H_{110}O_{12}}^{\text{Stearin.}}=3\ \overbrace{C_{36}H_{36}O_4}^{\text{Stearic acid.}}+\overbrace{C_6H_8O_6}^{\text{Glycerin.}}-3\ H_2O_2$$

And if glycerin be a triatomic alcohol, the composition of glyc and that of stearin may be represented as follows, on the typ 3 double molecules of water :—

$$\overbrace{\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_6}^{\text{Water.}}\quad;\quad\overbrace{\left.\begin{matrix}(C_6H_5)'''\\H_3\end{matrix}\right\}O_6}^{\text{Glycerin.}}\quad;\quad\overbrace{\left.\begin{matrix}(C_6H_5)'''\\(C_{36}H_{35}O_2)_3\end{matrix}\right\}O}^{\text{Stearin.}}$$

Intermediate between this triatomic alcohol, glycerin, which the only one of this series at present known, is a series of diato alcohols, the glycols, the existence of which was inferred by Wu and which by synthetic operations he succeeded in discoveri They are purely artificial bodies obtained from the hydrocarbons the olefiant gas series (1044).

The glycols yield compound ethers which are derived from t atoms of a hydrated acid and one of the glycol, so that they may represented as formed on the type of two double molecules of water

$$\overbrace{\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4}^{\text{Water.}}\quad;\quad\overbrace{\left.\begin{matrix}(C_4H_4)''\\H_2\end{matrix}\right\}O_4}^{\text{Glycol.}}\quad;\quad\overbrace{\left.\begin{matrix}(C_4H_4)''\\(C_4H_3O_2)_2\end{matrix}\right\}O_4}^{\text{Aceto glycolic ether.}}\quad;$$

$$\text{or}\qquad\overbrace{C_4H_6O_4}^{\text{Glycol.}}\quad;\quad\overbrace{C_4H_4O_2,\ 2\ C_4H_3O_3}^{\text{Binacetate of glycol.}}.$$

In the case of glycerin the tribasic radicle $(C_6H_5)'''$ which contains impresses its character upon the compound; whilst in glycols the dibasic hydrocarbon $(C_4H_4)''$ or one of its homolog imparts a dibasic constitution to the body.

The active study of the compounds of which glycerin glycol are the representatives, is daily bringing to light a multit of new bodies, and rapidly extending our views upon the consti tion of many organic bodies of very complicated composition.

For example, it appears to be very probable that mannite

Table of Isologous Groups.

Oxide.	Chloride.	Alcohol.	Aldehyd.	Volatile Acid.
(a) *Compounds of the Ethylic Series.*				
$C_{2n}H_{2n+1})_2O_2$	$(C_{2n}H_{2n+1})Cl$	$C_{2n}H_{2n+1}O,HO$	$(C_{2n}H_{2n-1}O_2,H)$	$HO,C_{2n}H_{2n-1}O_3$
Ether.	Hydrochlor. Ether	Alcohol.	Acetic Aldehyd.	Acetic Acid.
$(C_4H_5)_2O_2$	C_4H_5Cl	C_4H_5O,HO	$C_4H_3O_2,H$	$HO,C_4H_3O_3$
(b) *Compounds of the Allylic Series.*				
$C_{2n}H_{2n-1})_2O_2$	$C_{2n}H_{2n-1}Cl$	$C_{2n}H_{2n-1}O,HO$	$C_{2n}H_{2n-3}O_2,H$	$HO,C_{2n}H_{2n-3}O_3$
ide of Allyl.	Chloride of Allyl.	Allylic Alcohol.	Acrolein.	Acrylic Acid.
$(C_6H_5)_2O_2$	C_6H_5Cl	C_6H_5O,HO	$C_6H_3O_2,H$	$HO,C_6H_3O_3$
(c) *Compounds of the Benzoic Series.*				
$C_{2n}H_{2n-7})_2O_2$	$C_{2n}H_{2n-7}Cl$	$C_{2n}H_{2n-7}O,HO$	$C_{2n}H_{2n-9}O_2,H$	$HO,C_{2n}H_{2n-9}O_3$
	Chloride of Benzoene.	Benzoic Alcohol.	Oil of Bitter Almonds.	Benzoic Acid.
	$C_{14}H_7Cl$	$C_{14}H_7O,HO$	$C_{14}H_5O_2,H$	$HO,C_{14}H_5O_3$
				Toluic Acid.
				$HO,C_{16}H_7O_3$
		Cuminic Alcohol.	Oil of Cummin.	Cuminic Acid.
		$C_{20}H_{13}O,HO$	$C_{20}H_{11}O_2,H$	$HO,C_{20}H_{11}O_3$
(d) *Compounds of the Cinnamic Series.*				
		$C_{2n}H_{2n-9}O,HO$	$C_{2n}H_{2n-11}O_2,H$	$HO,C_{2n}H_{2n-11}O_3$
		Styrone.	Oil of Cinnamon.	Cinnamic Acid.
		$C_{18}H_9O,HO$	$C_{18}H_7O_2.H$	$HO,C_{18}H_7O_3$

) *Polybasic Alcohols.*—In addition to the various alcohols ı we have spoken, and which are all monobasic, and formed e type $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, we meet with others of more complicated tion formed upon the types of $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4$ and $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_6$, and of gher multiples of H_2O_2. Chevreul, when he published his r researches upon the fatty bodies, pointed out the analogy the fixed oils and fats, and the compound ethers; when under ence of bases they underwent saponification, they were decomposed with the assimilation of the elements of water into a fatty acid, and into glycerin, a body which in this respect presents an analogy with alcohol; but he did not see the precise difference, and the completeness of the parallel has only recently been established, and the distinction between the two pointed out. Berthelot, by synthetic experiments (1069) has shown that the neutral fats are derived from three atoms of a monobasic acid, and one atom of glycerin; glycerin being in fact a *triatomic alcohol*, and presenting a constitution which has its representative among the acids, in the tribasic phosphoric acid.

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Intermediate between this triatomic alcohol, glycerin, which is the only one of this series at present known, is a series of diatomic alcohols, the glycols, the existence of which was inferred by Wurtz, and which by synthetic operations he succeeded in discovering. They are purely artificial bodies obtained from the hydrocarbons of the olefiant gas series (1044).

The glycols yield compound ethers which are derived from two atoms of a hydrated acid and one of the glycol, so that they may be represented as formed on the type of two double molecules of water—

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In the case of glycerin the tribasic radicle $(C_6H_5)'''$ which it contains impresses its character upon the compound; whilst in the glycols the dibasic hydrocarbon $(C_4H_4)''$ or one of its homologues imparts a dibasic constitution to the body.

The active study of the compounds of which glycerin and glycol are the representatives, is daily bringing to light a multitude of new bodies, and rapidly extending our views upon the constitution of many organic bodies of very complicated composition.

For example, it appears to be very probable that mannite and sgars are polybasic alcohols, mannite and glucose being sibly hexatomic—

$$\left.\begin{matrix}H_6\\H_6\end{matrix}\right\}O_{12}\quad;\quad\overbrace{\left.\begin{matrix}C_{12}H_8\\H_6\end{matrix}\right\}O_{12}}^{\text{Mannite.}}\quad;\quad\overbrace{\left.\begin{matrix}C_{12}H_6\\H_6\end{matrix}\right\}O_{12}}^{\text{Glucose.}}\quad;$$

Each polyatomic alcohol has its hydrocarbon radicle, its correding ethers, its aldehyds, and its acids, and all these heterologous vatives from the alcohol are themselves, like it, polyatomic. A ral idea of the very numerous bodies which are correlated by this may be formed from an examination of the subjoined table:—

Type $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$ *Monatomic Alcohols and Derivatives.*					
rbon.	Alcohol.	Ether.	Aldehyd.	Acid.	Compound Ether.
yl. $H_5)_2$	Ethylic. $C_4H_6O_2$	Ethylic Ether. $(C_4H_5)'_2O_2$	Acetic. $C_4H_4O_2$	Acetic. $C_4H_4O_4$	Acetic Ether. $C_4H_5O,C_4H_3O_3$
yl. $H_7)_2$	Tritylic. $C_6H_8O_2$		Propionic. $C_6H_6O_2$	Propionic. $C_6H_6O_4$	Proportionate of Ethyl. $C_4H_5O,C_6H_5O_3$
Type $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4$ *Diatomic Alcohols and Derivatives.*					
ne. H_4	Glycol. $C_4H_6O_4$	Oxide of Ethylene. $(C_4H_4)''O_2$ Monethyl-Glycol. $HO,C_4H_5O,C_4H_4O_2$ Diethyl-Glycol. $(C_4H_5)_2O_2,C_4H_4O_2$	Glyoxal. $C_4H_2O_4$	Glycolic. $C_4H_4O_6$ Glyoxalic. $C_4H_2O_6$ Oxalic. $C_4H_2O_8$	Monacetate of Glycol. $HO,C_4H_4O_2,C_4H_3O_3$ Diacet. Glycol. $C_4H_4O_2,\ 2\,C_4H_3O_3$
ne. H_6	Trityl Glycol. $C_6H_8O_4$		Not yet formed.	Lactic. $C_6H_6O_6$ Wanting Malonic. $C_6H_4O_8$	Monacet. propyl Glycol. $HO,C_6H_6O_2,C_4H_3O_3$ Diacet propyl Glycol. $C_6H_6O_2,\ 2\,C_4H_3O_3$
Type $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_6$ *Triatomic Alcohols and Derivatives.*					
$H_5)'''$	Glycerin. $C_6H_8O_6$	Glyceric Ether. $(C_6H_5)_2'''O_6$ Diethylin. $HO(C_4H_5)_2O_2C_6H_5O_2$ Ethylin. $2\,HO,C_4H_5O,C_6H_5O_3$	Not yet formed.	Glyceric. $C_6H_6O_8$ Tartronic. $C_6H_4O_{10}$	Monacetin. $2\,HO,C_6H_5O_3,C_4H_3O_3$ Diacetin. $HO,C_6H_5O_3,\ 2\,C_4H_3O_3$ Triacetin. $C_6H_5O_3,\ 3\,C_4H_3O_3$

Although many of these polyatomic alcohols are artific bodies, yet the study of this class of compounds presents hig attractions to the chemist, as it is amongst these substances th many of the most interesting and extensively diffused natur compounds occur, as, for instance, the sugars, the different form of mannite, glycerin, and all its compounds in the natural fats a fixed oils.

(974) *Characters of the Alcohols of the group* $(C_{2n}H_{2n+2}O_2)$. The monobasic alcohols homologous with ordinary alcohol, formed either by a process of fermentation from sugar, as occ with ethylic, tritylic, tetrylic, amylic, and hexylic alcohol; by destructive distillation, as in the preparation of wood spirit; by treating certain fatty bodies with hydrate of potash, as the process of obtaining octylic, laurylic, cetylic, cerylic, and me sylic alcohols.

Many of the alcohols may also be formed synthetically by solving the diatomic hydrocarbons, such as ethylene and tritylene oil of vitriol, diluting the liquid and then distilling; thus

$$\overbrace{C_4H_4}^{\text{Ethylene.}}+\overbrace{2\,HO,S_2O_6}^{\text{Sulph. acid.}}+2\,HO=\overbrace{C_4H_6O_2}^{\text{Alcohol.}}+\overbrace{2\,HO,S_2O_6}^{\text{Sulph. acid.}};$$

or they may be obtained by causing a hydrocarbon of the ethyl series (1044) to combine with a hydracid, and then decomposing compound so obtained by long continued exposure to the action hydrate of potash. Berthelot has in this way obtained tritylic, amy octylic, and ethalic alcohols, by the reaction shown in the equati which follow :—

$$\overbrace{C_6H_6}^{\text{Tritylene.}}+HCl=\overbrace{C_6H_7Cl,}^{\text{Chloride of trityl.}}\text{ and}$$

$$\overbrace{C_6H_7Cl}^{\text{Chloride of trityl.}}+KO,HO=\overbrace{C_6H_8O_2}^{\text{Tritylic Alcohol.}}+KCl.$$

The alcohols present themselves in the form of liquids or so which are lighter than water. The lower terms of the series freely soluble in water, but they become less soluble as the portion of carbon and hydrogen increases, the higher terms of series becoming successively more viscid and oily, whilst th which are solid at ordinary temperatures are insoluble in wa and resemble the fats in appearance. The lower terms of series may be volatilized without experiencing decomposition. boiling point of each alcohol is about 72° lower than that of fatty acid which it yields by oxidation.

The following is a list of bodies at present known, wh belong to the class of substances homologous with vinic alcoh but there can be no doubt that as science progresses this list will be extended, and that ultimately an alcohol will be found corresponding to each term of the series of the volatile acids represented by the general formula, $HO,(C_{2n}H_{2n-1})O_3$:—

Alcohols.	Formula.	Specific Gravity.		Boiling point °F.
	$(C_{2n}H_{2n+2}O_2)$ or $(C_{2n}H_{2n+1}O,HO)$	Liquid.	Vapour.	
1. Wood spirit, or methylic alcohol .	$C_2H_4O_2$ or C_2H_3O,HO	0·798	1·12	149·9
2. Spirit of wine, or ethylic . . .	$C_4H_6O_2$ „ C_4H_5O,HO	0·7938	1·6133	173
3. Tritylic, or propylic .	$C_6H_8O_2$ „ C_6H_7O,HO		2·02	206
4. Tetrylic, or butylic .	$C_8H_{10}O_2$ „ C_8H_9O,HO			233
5. Fousel oil, or amylic	$C_{10}H_{12}O_2$ „ $C_{10}H_{11}O,HO$	0·8184	3·147	269·8
6. Hexylic, or caproic .	$C_{12}H_{14}O_2$ „ $C_{12}H_{13}O,HO$	0·833	3·53	299-309
7. Heptylic	$C_{14}H_{16}O_2$ „ $C_{14}H_{15}O,HO$	0·819		351
8. Octylic, or caprylic .	$C_{16}H_{18}O_2$ „ $C_{16}H_{17}O,HO$	0·823	4·5	356
12. Laurylic alcohol . .	$C_{24}H_{26}O_2$ „ $C_{24}H_{25}O,HO$			
16. Ethal, or cetylic . .	$C_{32}H_{34}O_2$ „ $C_{32}H_{33}O,HO$			
27. Cerotin, or cerylic .	$C_{54}H_{56}O_2$ „ $C_{54}H_{55}O,HO$			
30. Melissin, or melissylic	$C_{60}H_{62}O_2$ „ $C_{60}H_{61}O,HO$			

The formulæ of each of these substances, it will be seen, contains 2 atoms of oxygen, combined with quantities of carbon and hydrogen in which the number of atoms of hydrogen always exceeds by two, the number of atoms of carbon; an *even* number of atoms of carbon being always present. The alcohols may all be regarded as compound oxides of hydrogen and of a peculiar hydrocarbon, of which the general formula is $C_{2n}H_{2n+1}$, or as formed from a double molecule of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$ in which one-half of the hydrogen has been displaced by an equivalent of a hydrocarbon,—ordinary alcohol being represented upon this view as $\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2$. The other equivalent of hydrogen admits of being displaced by potassium, sodium, and other metallic bodies, and under certain circumstances by a second equivalent of a hydrocarbon either identical with or analogous to the first, thus giving rise to the simple or double ethers (989). The general formula of an alcohol, therefore, may be represented as $C_{2n}H_{2n+2}O_2$, or $(C_{2n}H_{2n+1})O,HO$. The alcohols by imperfect oxidation furnish *aldehyds;* and these bodies by the further absorption of oxygen yield *acids;* the latter in their hydrated form contain the same number of atoms of carbon as the alcohol from which they were procured, but 2 atoms less of hydrogen and 2 atoms more of oxygen, than the alcohol;

(*vide* table, page 35). These fatty acids may be obtained in combination with potash by heating the alcohol with hydrate of potash (980). The alcohols are further characterized by yielding, when treated with sulphuric acid and other dehydrating compounds, a class of substances termed *ethers*, which admit of being regarded as alcohols, minus 1 atom of water, though, as will hereafter be explained (989), there is reason to believe that this does not truly represent the mode of their formation.

(975) 1. Wood Spirit; *Methylic Alcohol*, or *Pyroxylic Spirit;* ($C_2H_3O,HO=32$): *Sp. Gr. of liquid at* 32° 0·8179; *of vapour* 1·12; *Boiling pt.* 140° Kane; 149° Kopp.—Wood spirit has not as yet been procured by any process of fermentation; it is found amongst the volatile products obtained by the destructive distillation of wood at a high temperature in closed vessels, accompanied by a large quantity of impure acetic acid, acetate of ammonia, acetate of methyl, tarry matter, and various hydrocarbons. It has also been obtained artificially by Berthelot, by acting upon marsh gas by chlorine, and decomposing the chloride thus obtained by means of a solution of potash.

Purification.—In order to isolate methylic alcohol, the crude products of the distillation of wood are rectified by the heat of a water bath, and the product is distilled from quicklime, which retains the acetic acid, the water, and tarry matter. The wood naphtha of commerce is simply rectified from chalk; as thus prepared it is a mixture consisting chiefly of methylic alcohol and acetate of methyl, with certain oily hydrocarbons insoluble in water. In order to free it from these impurities, the commercial spirit may be saturated with chloride of calcium, which forms with pyroxylic spirit a compound not decomposable at the temperature of boiling water: the mixture is subjected in a retort to the heat of a steam-bath, and the volatile portions are thus expelled. The residue, which retains the wood spirit, is mixed with an equal weight of water, by which the spirit is displaced from its combination with the chloride; and on renewing the application of heat, pyroxylic spirit, mixed with a little water, passes over; a second rectification from quicklime furnishes it in a state of purity.

Wöhler obtains wood spirit in a pure state more readily by converting it first into methyloxalic ether (1014) which being a solid may be purified by crystallization; when this ether is simply distilled with water, it is converted into oxalic acid and wood spirit: the latter may then be rectified from quicklime, by which means it is obtained pure and in the anhydrous form.

Properties.—Wood spirit is a limpid, inflammable, colourless liquid, of a penetrating spirituous odour, and a disagreeable burning taste; the empyreumatic smell commonly observed is due to impurities in the product. It has a sp. gr. of 0·798 at 68°. It is soluble in water, alcohol, and ether, in all proportions. It is very inflammable, and burns with a pale flame, furnishing carbonic acid and water. When pure it does not reduce the subnitrate of mercury if mixed with its solution. Pyroxylic spirit mixes readily with the essential oils, and dissolves many fatty bodies and resins with facility. Its principal application in the arts, as crude wood naphtha, is founded upon its power of dissolving the resins, which, when thus dissolved, are employed as varnishes. A solution of shell-lac, and other resins in wood naphtha, is extensively used for stiffening the basis of silk hats. The hydrates of the alkalies are soluble in wood spirit, but they immediately colour it brown. Ure used this reaction as a means of discovering small quantities of pyroxylic spirit when mixed with alcohol; since alcohol is not thus altered in colour until after a considerable lapse of time. Caustic baryta is soluble in wood spirit, forming with it a crystallizable compound, BaO, $C_2H_4O_2$; and many salts form definite compounds with it; that with chloride of calcium (CaCl, 2 $C_2H_4O_2$) crystallizing in six-sided tables.

It has already been mentioned that when alcohol is submitted to a gradual and incomplete oxidation, one of the products of the operation is aldehyd (1077), which passes, by further oxidation, into acetic acid. Now, wood spirit may in like manner be subjected to partial oxidation, under the influence of finely divided platinum; and, though the different stages of the process have been less satisfactorily investigated than those which occur with ordinary alcohol, it appears that an intermediate substance is formed, which, like aldehyd, has the power of reducing the salts of silver; and finally, a strong solution of formic acid is produced. This acid stands in the same relation to the methylic series that the acetic does to the ethylic series:—

$$\overbrace{C_4H_5O,HO}^{\text{Alcohol.}}+O_4 = \overbrace{HO,C_4H_3O_3}^{\text{Acetic Acid.}}+H_2O_2\,;$$

$$\overbrace{C_2H_3O,HO}^{\text{Wood Spirit.}}+O_4 = \overbrace{HO,C_2HO_3}^{\text{Formic Acid.}}+H_2O_2.$$

This method, however, is not an advantageous one for the preparation of formic acid, since it is difficult to prevent the oxidation from going a stage further, and converting the formic acid into carbonic acid and water;

$$2\,(HO,C_2HO_3)+O_4 = 2\,H_2O_2+2\,C_2O_4.$$

When wood spirit is heated moderately with soda-lime, formiate of the base is produced, and hydrogen is liberated :—

$$\overbrace{HO,C_2H_3O}^{\text{Wood spirit.}} + NaO,HO = \overbrace{NaO,C_2HO_3}^{\text{Formiate of soda.}} + 2\ H_2.$$

If caustic potash be employed instead of soda-lime, oxalate of potash is formed, whilst a larger evolution of hydrogen occurs :—

$$2\ \overbrace{(HO,C_2H_3O)}^{\text{Wood spirit.}} + 2\ (KO,HO) = \overbrace{2\ KO,C_4O_6}^{\text{Oxal. potash.}} + 5\ H_2.$$

(976) 2. ALCOHOL ; *Ethylic or Vinic Alcohol ; Spirit of Wine* ($C_4H_6O_2=46$) : *Sp. Gr. of liquid at* 32°, 0·815 ; *of vapour* 1·6133 ; *Boiling pt.* 173°.—Alcohol is a colourless volatile inflammable liquid, of an agreeable well-known spirituous odour, and an acrid burning taste. When pure it has a specific gravity of 0·7938 at 60°. It has never been frozen, though at a temperature of —166° it becomes viscid. When taken in small quantities in a diluted form it furnishes a useful and well-known stimulant, forming the basis of all fermented liquors. In large quantities it produces intoxication, and acts as a powerful narcotic poison, frequently occasioning fatal results when taken in a concentrated state and in excess.

Alcohol furnishes a cleanly and valuable fuel to the chemist : it emits a high temperature during its combustion, and deposits no soot upon cold bodies which are introduced into its flame. When burned in air it emits but little light, and is wholly converted into carbonic acid and water : 4 volumes, or 1 molecule of alcohol vapour, for complete combustion requires 3 times its bulk, or 12 atoms of oxygen ; $C_4H_6O_2+3\ O_4=2\ C_2O_4+3\ H_2O_2$. When the vapour of alcohol is transmitted through red-hot tubes it is decomposed. The products vary according to the temperature employed ; at low temperatures, olefiant gas, marsh gas, water, carbonic oxide, and acetylene are formed ; and at higher temperatures, naphthalin ; whilst at a bright-red heat carbon is deposited, and free hydrogen produced. By gradual oxidation alcohol yields amongst other bodies, aldehyd and acetic acid (1078). With nitric acid it furnishes nitrous ether, glyoxal, glyoxalic acid (1129), with glycolic (1137) and oxalic acids.

When alcohol is exposed in its concentrated form to the atmosphere it attracts moisture, like sulphuric acid ; and like this compound, when mixed with water, it emits heat and contracts in bulk, though to a considerably less extent ; the observed density of the mixture of alcohol and water is therefore greater than its calculated mean density. According to Rudberg, the condensation is greatest when 53·739 measures of alcohol and 49·836 of water are mixed at 59°: these proportions correspond to $C_4H_6O_2+3\ H_2O_2$; when cooled again to 59°, this mixture occupies only 100 measures instead of 103·575, and has a sp. gr. of 0·927. From the importance of alcohol as an exciseable article, great labour has been bestowed upon the means for readily determining its per-centage in spirituous liquors: the method in common use for distilled spirits consists in determining the specific gravity by means of a sensitive hydrometer, and tables have been constructed for showing the per-centage of alcohol in mixtures of various densities. In these cases great attention must be paid to the temperature, since slight differences in this particular make a material variation in the density. The term *proof spirit*, in constant use among the excise, is defined by an Act of Parliament (58 George III.), to be "such as shall at the temperature of 51° F. weigh exactly twelve thirteenth parts of an equal measure of distilled water." It consists of water 50·76, alcohol 49·24 by weight, and indicates alcohol of sp. gr. 0·920 at 60° (Drinkwater 0·91984). The term derives its origin from the rude method of proof formerly in use, in which gunpowder was moistened with the spirit of wine to be tried, and the alcohol ignited; if it fired the powder it was said to be *over proof*, but if the spirit burned off and left the powder damp, it was considered to be *under proof;* the weakest spirit capable of thus firing powder had a sp. gr. of about 0·920.*

Alcohol is a solvent of great value to the chemist. It usually exerts but little chemical action upon the bodies which it dissolves, and owing to its volatility it is easily expelled by a gentle heat, leaving the substances which it previously held in solution in a pure state. Alcohol dissolves many of the gases freely; some of them, as for instance, protoxide of nitrogen, carbonic acid, phosphuretted hydrogen and cyanogen, are dissolved by it more readily than by water. Iodine and bromine are also readily soluble in it, but their solutions gradually undergo decomposition, in consequence of the reaction of iodine and bromine upon the alcohol. Absolute alcohol dissolves small quantities of phosphorus and of sulphur. The alkaline sulphides, as well as caustic potash and soda, are soluble in it to a very large extent; and ammoniacal gas is absorbed by it nearly as readily as by water; but it does not dissolve the carbonates of these alkalies. Alcoholic solutions of caustic potash and soda act powerfully as reducing agents upon many metallic solutions, such as those of platinum; they gradually absorb oxygen from the air, and become brown, owing to the formation of a resinoid substance.

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* In the Appendix two tables of the strength of alcohol at different specific gravities will be found.

Most of the deliquescent salts are soluble in alcohol, but the efflorescent salts, and those which are sparingly soluble in water, are not dissolved by it. Anhydrous alcohol combines with many anhydrous saline bodies in definite proportions, and forms with them crystallizable compounds, in which the alcohol, according to Graham, occupies the place of water of crystallization. The chlorides and the nitrates offer the best examples of the formation of these *alcoates*. The compound with chloride of calcium ($CaCl + 2\,C_4H_6O_2$), crystallizes readily; and analogous compounds may be obtained with the chlorides of zinc and manganese, and with the nitrates of lime and magnesia.

Alcohol likewise dissolves many organic bodies freely, such as the resins, the essential oils, the vegetable alkaloids, and many of the vegetable acids. It also dissolves more sparingly, sugar, and the soaps of potash, soda, and ammonia; but the fats and fixed oils, with the exception of castor oil, are dissolved by it in but small quantities.

A characteristic reaction of alcohol is its power of forming fulminate of silver; when 1 grain of silver is dissolved in 20 grains of nitric acid, and about 50 of alcohol are added, crystals of fulminate of silver are gradually deposited.

The results of the action of chlorine (1017) and of sulphuric and other acids, as well as of sodium and other metals (1024 *et seq.*) upon alcohol, will be alluded to hereafter.

Preparation.—Alcohol may be obtained in a state of purity by subjecting to distillation any saccharine solution that has undergone fermentation; for being more volatile than water it passes over in the first part of the distillation, accompanied with more or less water. By repeated rectifications, or by a single operation in Coffey's still (175), it may be concentrated till it contains about 10 per cent. of water. Beyond this point the water adheres to it so strongly that it requires a different process for the complete separation of the last portions:—it is first rectified from charcoal, with a view of retaining all essential oils to which the peculiar odour and flavour of different spirits are mainly owing, and is then mixed with about half its weight of quicklime, and allowed to stand for three or four days: the lime gradually slakes and falls to powder in consequence of its conversion into a hydrate, at the expense of the water in the alcohol; then, on applying heat by means of a bath of chloride of calcium, the pure spirit may be distilled off, the hydrate of lime retaining the water at temperatures far above 300° F. Any traces of water which it may still retain are removed by a second distillation from quicklime, or from caustic baryta. The alcohol thus obtained is anhydrous, or as it is often termed, *absolute alcohol*.*

Berthelot (*Ann. de Chimie*, III. xlv. 385) has pointed out a means of obtaining alcohol synthetically, by forming a solution of olefiant gas in oil of vitriol, which dissolves about 120 times its bulk of the gas, then diluting the mixture and submitting it to distillation. Small quantities of dilute alcohol are thus obtained with facility.

Tritylic alcohol has been obtained by acting on tritylene in a similar manner, but the denser hydrocarbons of this series, such as octylene, become charred when thus treated.

(977) *Wines, Fermented Liquors, and Spirits.*—The various kinds of spirits in use derive their names from accidental circumstances, often from the flavour which they possess. Thus, *gin* is spirit flavoured by distilling it with juniper berries; *peppermint* owes its aroma to the essential oil of the plant after which it is named; *whiskey* is spirit distilled from wort prepared from malt which has been dried over a peat fire, to which its peculiar flavour is due; *arrack* is a spirit distilled from fermented rice; and *rum*, a West Indian product from molasses; *brandy* is really the spirit of wine, being obtained from wines by distillation, and coloured more or less deeply with burnt sugar. In all these cases the characteristic flavour depends upon a small quantity of some volatile oil or compound ether which passes over with the spirit during the process of distillation.

The varieties of spirits are very numerous, and those of fermented liquors which are used without subjecting them to distillation, are still greater. To this class belong all the different kinds of wine, which owe their peculiarities of flavour partly to the different varieties of grape, of which 500 or 600 are cultivated, and partly to the different flavour which even the same variety of grape† possesses in different climates, according as the saccharine, the aromatic, the acidulous, or the astringent principle of the fruit predominates, the grapes grown in the hottest climates furnishing the sweetest juice, but not the wines of finest quality; the flavour is also materially influenced by the manner in which the wine is prepared. For example, when fermentation is allowed to proceed until all the sugar is transformed into spirit, a dry wine is produced; when checked before this term is reached, the result is a rich fruity wine: and when bottled whilst the fermentation is still proceeding, a brisk effervescent wine like champagne is the result. It is the usual practice to add cane sugar to champagne before bottling. According to the experiments of Bence Jones, claret, Burgundy, and the wines of the Rhine and the Moselle, contain no sensible quantity of sugar; sherry yields from 1 to 5 per cent., port from 3 to 7 per cent., and Tokay as much as 17 per cent. of sugar. The ageing of wine and consequent change of flavour, depends partly upon the gradual fermentation of sugar still retained in rich wines, and partly upon the slow separation of saline matter, principally in the form of bitartrate of potash, which becomes less soluble as the proportion of spirit increases, and is deposited, particularly from port wines, as a crust of tartar, upon the sides of the bottle. An important part of the change of flavour appears also to be owing to the slow formation of minute quantities of fragrant and aromatic ethers which are gradually produced by the reaction of the vegetable acids upon the alcoholic portion of the wine. It has been observed that the presence of a considerable amount of acidity favours the development of the 'bouquet' or aroma, which is especially characteristic of the acidulous wines of the Rhine and the Moselle.

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* The methylated spirit of commerce consists of a mixture of alcohol of sp. gr. 0·830 with 10 per cent. of wood spirit. This addition of wood spirit renders it unfit for use afterwards as a stimulant drink; it was added to facilitate the use of spirit in the arts without inflicting injury on the revenue, as the contamination cannot be removed by any known process of purification, though it scarcely interferes with the employment of the spirit as a solvent.

† A certain variety of grape when grown upon the Rhine furnishes a species of Hock; the same grape when raised in the valley of the Tagus yields Bucellas; whilst in the island of Madeira it produces the wine known as Sercial, which has a flavour quite different from either of the others.

Some wines instead of improving, become ropy by keeping. This occurs only with sweet wines, and is due to a peculiar species of fermentation in which the sugar passes into the uncrystallizable form of mucilage (952, 970).

The colour of the wine is dependent upon the mode in which the fermentation is effected. Red grapes may be made to yield a 'white' wine, if the husks of the grape be removed from the must before the fermentation begins, as in the preparation of champagne and sherry; but if the skins be left in the fermenting mass, the alcohol, as it is formed, dissolves the colouring matter, producing the different shades of 'red' wine. During the preparation of red wines the skins and stalks rise to the surface of the fermenting mass and form the *chapeau*, which is removed from the fermenting juice at an earlier stage in the making of clarets than in the preparation of ports, and this is one reason why port is the more astringent wine of the two.

The process of fermentation in making wine is much more gradual and protracted than in the preparation of malt liquors. After the grapes have been trodden in the press the juice passes to the fermenting vessels; no addition of yeast is necessary, and after a short time a copious deposit of ferment granules or yeast occurs spontaneously. The fermenting vats are so constructed that when the active stage of the fermentation is over, they can be loosely closed by a bung. As soon as the winter frosts set in, the wine is decanted from the lees into casks, which are completely filled, and then closed with care. In order to supply the loss from leakage or evaporation, the casks are carefully filled up at intervals. Here a secondary very gradual fermentation occurs. It requires careful watching, exclusion of the air at this stage being indispensable in order to prevent the wine from becoming sour owing to the formation of acetic acid by the oxidation of the alcohol.

Sometimes a wine acquires a peculiar flavour known as the "taste of the cask." This is attributed to the development of a peculiar essential oil during the growth of fungi, or 'mould,' upon the surface of the wine. It is said that it may be removed by adding to each pipe about a quart of olive oil, which dissolves the obnoxious flavouring matter, and carries it with it to the surface.

It is obvious that in wines and other fermented liquors which have not been submitted to distillation, all the soluble matter of the fruit is present in the beverage. Other saccharine juices, besides those of the grape, admit of being fermented, and thus a great variety of drinks may be produced. Beer and ale, for example, consist of an infusion of malt, flavoured by the aromatic bitter of the hop, and subsequently fermented. The different kinds of porter are similarly prepared, and owe their dark colour to the use of high-dried malt: *cider* is the fermented juice of the apple; *perry* is a similar liquid obtained from the pear; and nearly every fruit may be made to yield its own peculiar liquor. Even savage nations evince a knowledge of this fact. The natives of the islands in the Pacific, when discovered by Cook, not only knew how to prepare an intoxicating liquor from the juice of the cocoa-nut, but they were accustomed to rectify it by a rude process of distillation.

Since foreign matters are present in all fermented liquors, the specific gravity would, except in special cases,* be no guide to the quantity of spirit contained in them. A simple means of ov coming this difficulty was successfully practised by Brande: Carbonate of potash is soluble in water, but insoluble in alcoho when perfectly dry carbonate of potash is poured into a mixture alcohol and water, the salt becomes dissolved in the water, and th liquid separates into two layers, the upper of which consists alcohol of sp. gr. 0·825. By employing a graduated tube for th experiment, the volume of alcohol which is contained in any wi or liquor may be read off at once by inspection.

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* See "Report on Original Gravities" by Graham, Hofmann, and Redwood (*Q. J. Chem. Soc.* v. 229).

Christison submitted different wines to distillation, in order determine their percentage of alcohol; he thus obtained a seri of results, the most important of which are embodied in the fo lowing table. The numbers represent the weight of absolu alcohol contained in 100 parts of each variety of wine or ferme liquor:—

Port . . .	from 14·97 to 17·10	Amontillado .		12·63	
Dry Lisbon .	16·14	Claret . . .	from	7·72	to 8·9
Madeira . .	from 14·09 to 16·90	Hambacher .		7·35	
Sherry . .	„ 13·98 „ 16·17	Rudesheimer .	from	6·90	to 8·
Teneriffe . .	13·64	Edinburgh ale	„	5·70	„ 6·0
Shiraz . .	12·95	Best London porter .		5·36	
Malmsey . .	12·86				

(978) 3. *Tritylic* (or *propylic*) *Alcohol* (C_6H_7O,HO); *Sp. gr.* *liquid* 0·817; *of vapour* 2·02; *Boiling pt.* about 206°.—Althou during the ordinary process of the fermentation of fruit or gra sugar, the products are carbonic acid and ordinary (ethylic) alcoh it usually happens that minute quantities of other homologo bodies are formed. This is particularly the case when masses the husk of the grape, from which the juice has been expres (technically termed the *marc* of the grape), are thrown aside, a allowed to ferment. The saccharine matter which they still reta undergoes decomposition, and when the fermented liquor furnish by them is submitted to distillation, a mixture of tritylic, tetry (butylic), amylic, and hexylic (caproic) alcohol is obtained.

These different modes of fermentation admit of explanation means of the following equations, in which it is assumed that addition to the separation of carbonic acid, a certain quantity water is eliminated at the same time:—

$$2\,\overbrace{C_{12}H_{12}O_{12}}^{\text{Sugar.}} = 4\,\overbrace{C_2O_4}^{\text{Carb. acid.}} + H_2O_2 \;+\; \overbrace{\overbrace{C_4H_6O_2}^{\text{Ethylic.}} + 2\,\overbrace{C_6H_8O_2}^{\text{Tritylic.}}}^{\text{Alcohols.}};$$

$$2\,C_{12}H_{12}O_{12} = 4\,C_2O_4 + 2\,H_2O_2 + 2\,\overbrace{C_8H_{10}O_2}^{\text{Tetrylic.}};$$

$$\overbrace{2\,C_{12}H_{12}O_{12}}^{\text{Sugar.}}=\overbrace{4\,C_2O_4}^{\text{Carb. acid.}}+2\,H_2O_2+\overbrace{\overbrace{C_6H_8O_2}^{\text{Tritylic.}}+\overbrace{C_{10}H_{12}O_2}^{\text{Amylic.}}}^{\text{Alcohols.}};$$

$$2\,C_{12}H_{12}O_{12}=4\,C_2O_4+2\,H_2O_2+\overbrace{C_4H_6O_2}^{\text{Ethylic.}}+\overbrace{C_{12}H_{14}O_2}^{\text{Hexylic.}}.$$

ylic alcohol, the third term of the alcoholic series, is obtained in small quantity from the fermented marc. It may also be ared by Berthelot's process of absorbing tritylene by oil of ol, diluting the solution with 5 or 6 times its bulk of water distilling. It is a limpid, colourless liquid, lighter than water, an agreeable fruity odour. Although freely soluble in water, es not mix with it in all proportions.

(979) 4. *Tetrylic* (or *butylic*) *Alcohol* (C_8H_9O,HO) : *Sp. gr. of id* 0·8032 ; *of vapour* 2·589 ; *Boiling pt.* 233°.—Wurtz procured fourth term of the alcohols during the rectification of fousel oil ined from beet-root spirits ; it is contained in that portion which below 266°. By fractional distillation this portion may be e to yield a liquid, the boiling point of which remains steady 33°, and which is the desired alcohol. Tetrylic alcohol is a urless liquid of high refracting power, lighter than water, and partially soluble in water. It has an odour resembling that usel oil, but less oppressive. When heated with the hydrate otash, it is readily converted into butyrate of potash, with tion of hydrogen ; and, when mixed with concentrated sul- ic acid, it forms *sulphotetrylic* (or *sulphobutylic*) acid (HO, H_9O,S_2O_6) without difficulty.

(980) 5. AMYLIC ALCOHOL, *Fousel Oil* or *Potato Spirit* $H_{11}O,HO=88$) ; *Sp. gr. of liquid* (*at* 32°) 0·827 : *of vapour* 47 ; *Boiling pt.* 269°·8 (Kopp).—This substance, which consti- the fifth term of the alcohol series, is a frequent impurity in ies distilled from fermented potatoes, barley, rye, and the e of grapes, to which it communicates a peculiar offensive odour taste. Since it is considerably less volatile than either alcohol water, it accumulates in the last portions of the liquid when h brandies are submitted to distillation. Crude fousel oil is ally mixed with a variable amount of different ethers of the ds of the acetic series.

According to Liebig (*Familiar Letters*, 4th ed. p. 217), fousel is formed principally in the fermentation of alkaline or neutral ids, and its production in the potato mash may be prevented, great measure, by adding crude tartar to the fermenting liquid.

Its formation, he says, never occurs in acidulous fermenting which contain tartaric, racemic, or citric acid. The addition to the liquid has a similar effect in checking the developm fousel oil.

Amylic alcohol is a colourless, limpid liquid, which has sistent, penetrating, and oppressive odour, and a burning ta is but sparingly soluble in water, though it may be mix alcohol, ether, and the essential oils, in all proportions. Its is very irritating when respired; it burns with difficulty bluish flame. The specific gravity of fousel oil at 59° is At about −4° it congeals into crystalline plates. Amylic causes a left-handed rotation of the plane of polarization i of polarized light, but the extent of this power varies gre different specimens. According to Pasteur, ordinary amylic consists of a mixture of two metameric bodies, one of w inactive on polarized light, but the other produces left- rotation of a polarized ray. The two modifications can b rated by converting the alcohol into sulphamylic acid, an oining this with baryta. Both the sulphamylates of crystallize in the same form, but the inactive variety requ times as much water for its solution as the active one. Th alcohol has a sp. gr. about $\frac{1}{100}$th greater than the inactive and it boils between 260°·6 and 262°·4. The inactive boils at 264°·2.

Under the influence of spongy platinum, amylic alcohol ally absorbs oxygen, whilst hydrogen is eliminated in the water, and valeric acid is produced; this acid bears the san tion to amylic alcohol that acetic acid does to ordinary alc

$$\overbrace{C_{10}H_{12}O_2}^{\text{Fousel oil.}}+O_4=\overbrace{HO,C_{10}H_9O_3}^{\text{Valeric acid.}}+H_2O_2.$$

The action of nitric acid upon amylic alcohol varies w degree of its concentration and the temperature of the n as it may be made to yield nitrate of amyl, valeric acid, of amyl, or valeric aldehyd. Hydrate of potash is freely in fousel oil. If fousel oil be heated on a mixture of hyd potash and lime to 430°, valerate of potash is formed, hydrogen is liberated:—

$$C_{10}H_{12}O_2+KO,HO=KO,C_{10}H_9O_3+2\ H_2.$$

When heated with phosphoric acid, or with chloride of zinc oil yields hydrocarbons homologous with olefiant gas. mixed with half its bulk of sulphuric acid the mixture b hot, assumes a red colour, and a viscid consistence, a large quantity of *sulphamylic* acid being formed, the amount of which increases if the mixture be allowed to stand for 24 or 48 hours. The sulphamylates crystallize with difficulty and form syrupy solutions.

(981) 6. *Hexylic* or *Caproic Alcohol* ($C_{12}H_{14}O_2$): *Sp. gr. at* 32° 0·833; *of vapour* 3·53.—This compound has also been obtained from the fermented marc of the grape. It is a limpid, aromatic liquid, which is insoluble in water, and boils between 299° and 309°. It yields caproate of potash, with disengagement of hydrogen, when heated with hydrate of potash; caproic acid standing in the same relation to hexylic alcohol that acetic acid does to ordinary alcohol.

7. *Œnanthylic Alcohol* ($C_{14}H_{16}O_2$: *Sp. gr. of liquid* 0·819; *Boiling pt.* 351°) is obtained, according to Stœdeler, by distilling a mixture of hydrate of soda with the ricinoleate of this base in a copper retort. Sebate of soda is left in the retort, and the distillate is treated with bisulphite of soda to separate the aldehyds; the liquid portion is removed by pressure, and after standing over chloride of calcium is rectified: the greater portion distils between 350° and 352°. It is a transparent, rather viscous liquid, which smells like œnanthol.

(982) 8. *Octylic*, or *Caprylic Alcohol* ($C_{16}H_{18}O_2$): *Sp. gr. of liquid* 0·823 at 62°; *of vapour* 4·5; *Boiling pt.* 356°.—This substance occurs in small quantity in the fermented marc of the grape, but its most interesting and available source is castor oil (Bouis, *Ann. de Chimie*, III. xliv. 100). Castor oil consists principally of the glycerin compound of a peculiar acid, *ricinolic acid* (1052), the formula for the latter in its hydrated state being ($HO,C_{36}H_{33}O_5$). This acid, when heated with an excess of hydrate of potash to about 480°, undergoes decomposition; sebate of potash being formed whilst octylic alcohol and hydrogen are liberated, as shown by the following equation:—

$$\overbrace{HO,C_{36}H_{33}O_5}^{\text{Ricinolic acid.}} + 2(KO,HO) = 2\,\overbrace{KO,C_{20}H_{16}O_6}^{\text{Sebate of potash.}} + \overbrace{C_{16}H_{18}O_2}^{\text{Octylic Alcohol.}} + H_2.$$

In order to isolate the alcohol, the castor oil is saponified by means of potash or soda, and afterwards an excess of the hydrated alkali, amounting to about half the weight of the oil operated upon, is added. The mass is heated moderately in a retort. It froths up at first considerably; but the foam gradually subsides, and a fragrant oily liquid distils over, which collects in the receiver above the water by which it is accompanied. The residue in the retort may be employed for the preparation of sebacic acid (1135). This distilled oil, which usually amounts to from a fourth to a fifth of the weight of the oil operated upon, must be purified by repeated rectifications from hydrate of potash, until the residue no longer has a brown colour.

Octylic alcohol is a colourless liquid, of a powerful, persistent, aromatic odour: it leaves a greasy stain upon paper, is insoluble in water, but freely soluble in alcohol and ether, as well as in acetic acid. It dissolves fatty and resinous bodies with facility. It undergoes no change when exposed to the air; but, when heated sufficiently, takes fire and burns with a white luminous flame. Sulphuric acid combines with the alcohol, and forms *sulphocaprylic*, or *sulphoctylic* acid, which yields crystallizable salts. Bouis has obtained a large number of compound and double ethers with this alcohol; some of them are very fragrant and aromatic.

Other alcohols will be alluded to in speaking of the fats (1054, 1055, 1125), under the heads of ethal, cerylic, and melissylic alcohol.

§ II. ACTION OF THE ACIDS UPON THE ALCOHOLS.

(983) WHEN a hydrated acid is mixed with one of the alcohols, several cases may arise, dependent on the nature of the acid, the proportions in which it is added, and the temperature applied to the mixture.

1st. If a polybasic acid which has a strong affinity for water, such as the sulphuric,* the phosphoric, or the arsenic, be added to one of the alcohols, the elements of the acid and of the alcohol enter into combination and form a new compound acid; a *vinic acid* being produced, in quantity varying with the temperature and relative proportions of the acid and the alcohol.

2nd. If such a mixture be submitted to distillation, the alcohol is decomposed, and a quantity of ether is formed and volatilized; whilst the residue in the retort is capable of effecting the etherification of fresh portions of alcohol.

3rd. If the proportion of acid to the alcohol exceed a certain amount, or if the temperature at which the distillation is effected rise beyond a certain point, the decomposition proceeds further, and one of the hydrocarbons homologous with olefiant gas is formed: whilst at still higher temperatures the acid originally used begins to undergo decomposition, and the products are still more complicated.

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* In considering the action of sulphuric acid upon organic compounds, we shall proceed throughout upon the assumption that it is dibasic, and that its formula is $2\,HO,S_2O_6$. In like manner carbonic acid will be viewed as dibasic, with a formula C_2O_4.

4th. When an organic acid is submitted to distillation with one of the alcohols, a double decomposition occurs, and a compound ether is produced, whilst the elements of water are separated; thus,

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2}^{\text{Acetic acid.}}+\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}=\overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_5\end{matrix}\right\}O_2}^{\text{Acetic ether.}}+\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}}.$$

It is generally found advisable in such cases to use a salt of the organic acid, and after this salt has been mixed with a due proportion of alcohol, to decompose it by the addition of sulphuric acid.

5th. If a hydracid, such as the hydrochloric, hydrobromic, or hydriodic, be made to act upon an alcohol, double decomposition occurs, and an ether is formed by the substitution of the radicle of the alcohol for the hydrogen of the hydracid; thus, when hydrochloric acid acts upon alcohol, water and hydrochloric ether are the result:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}+\overbrace{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}^{\text{Hydrochloric acid.}}=\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}}+\overbrace{\left.\begin{matrix}C_4H_5\\Cl\end{matrix}\right\}}^{\text{Hydrochloric ether.}}.$$

The Vinic Acids.

(984) When a mixture of concentrated sulphuric acid with any of the alcohols is heated to about 212°, a portion of the two compounds enters into combination, and the result is the formation of a new coupled acid in which the elements of 1 molecule of the alcohol and 1 of sulphuric acid (S_2O_6) are present. In these compounds the existence of sulphuric acid is no longer indicated by the formation of an insoluble sulphate of baryta on the addition of chloride of barium; the baryta salt of these acids being readily soluble in water.

The following may be taken as examples of a few of the compound acids thus obtained:—

Name of Acid.	Hydrate.	Potash Salt.
Sulphomethylic . . .	HO,C_2H_3O,S_2O_6	KO,C_2H_3O,S_2O_6+Aq
Sulphethylic, or sulphovinic	HO,C_4H_5O,S_2O_6	KO,C_4H_5O,S_2O_6
Sulphotritylic (propylic)	HO,C_6H_7O,S_2O_6	KO,C_6H_7O,S_2O_6
Sulphotetrylic (butylic)	HO,C_8H_9O,S_2O_6	KO,C_8H_9O,S_2O_6
Sulphamylic	$HO,C_{10}H_{11}O,S_2O_6$	$KO,C_{10}H_{11}O,S_2O_6+Aq$
Sulphoctylic	$HO,C_{16}H_{17}O,S_2O_6$	$KO,C_{16}H_{17}O,S_2O_6+Aq$

These acids form crystallizable salts with potash, as well as with lime, baryta, and many other bases; but the salts thus formed are unstable, and sometimes undergo spontaneous decomposition; the salts of these acids have a peculiar pearly lustre. It is important to remark, that although the acid contains the elements of one molecule or two equivalents of sulphuric acid, the salts are monobasic, and contain only one equivalent of a metallic protoxide, as may be seen by inspecting the column headed 'potash salt.'

The hydrates of these sulpho-acids are more unstable than their metallic salts; they cannot be distilled without undergoing decomposition, and they then break up into the ether corresponding to the alcohol which furnished them, and sulphuric acid. If diluted with water and heated, the solution becomes rapidly converted into a mixture of diluted sulphuric acid, and the alcohol from which the compound was originally obtained: for instance,

$$\overbrace{HO,C_4H_5O,S_2O_6}^{\text{Sulphethylic acid.}}+H_2O_2=\overbrace{HO,C_4H_5O}^{\text{Alcohol.}}+2\ \overbrace{HO,S_2O_6}^{\text{Sulphuric acid.}}.$$

The most interesting of these acids is the sulphethylic, and it is necessary to examine its properties, on account of the prominence which has been assigned to it in the theory of etherification.

(985) *Sulphethylic*, or *Sulphovinic Acid* ($C_4H_6O_2,S_2O_6=HO,C_4H_5O,S_2O_6$).—When alcohol is mixed with an equal measure of oil of vitriol, great heat is evolved, and the two bodies enter partially into combination.* The sulphuric acid thus combined with the elements of alcohol, loses half its saturating power, and the compound acid, when diluted with 5 or 6 times its bulk of water, may be neutralized by the gradual addition of baryta, lime, or oxide of lead. The base should be mixed with water till of the consistence of a thin cream: the salts thus formed are soluble in water. By adding sulphuric acid gradually to a solution of the baryta salt, until no further precipitate of sulphate of baryta is produced, the acid is set at liberty in a state of purity. It was originally called the *sulphovinic acid*, but the term *sulphethylic*, by which it is now frequently described, is better, as it forms one

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* In order to produce the largest amount of the compound acid, the mixture should be heated to about 260° for a short time, and then allowed to stand for 24 hours. But the alcohol is never wholly converted into the new acid, for even if anhydrous alcohol be mixed in the above proportions with monohydrated sulphuric acid, not more than half the alcohol becomes converted into the vinic acid, since, in the act of combination, a portion of water is displaced from the oil of vitriol; and on applying a heat of 212°, diluted alcohol gradually passes over, though the liquid does not boil at this temperature.

of a numerous class of analogous acids. Sulphethylic acid may also be formed by gradually adding ether, perfectly free from alcohol, to concentrated sulphuric acid; the temperature rises rapidly, but must not be allowed to exceed 250°: on diluting the mixture with water it will be found that much of the ether has been converted into sulphethylic acid. It is worthy of notice in connexion with the theory of etherification (993), that when alcohol is mixed with sulphuric acid, diluted till of sp. gr. 1·53 ($= 2\,HO, S_2O_6 + 6\,Aq$), no sulphethylic acid is formed at ordinary temperatures, but this acid is produced if the temperature be raised to 212°.

The hydrated acid is very unstable. If diluted with water and distilled, alcohol passes over, and sulphuric acid is left in the retort; but the diluted sulphethylic acid may be concentrated over sulphuric acid in vacuo, when it forms a colourless syrupy liquid, of a sharp acid taste, not miscible with ether. It gradually undergoes spontaneous decomposition. When heated in the presence of an excess of alcohol, it experiences a remarkable decomposition, to which it will be necessary to give particular attention (993), owing to its connexion with the formation of ether.

All the sulphethylates are freely soluble in water; many of them are likewise dissolved by alcohol; most of these salts crystallize with facility in pearly scales which feel greasy to the touch. When subjected to dry distillation, they yield olefiant gas, heavy oil of wine, and sulphurous and carbonic acids, leaving a residue of sulphate of the base, mixed with charcoal. If distilled with hydrate of potash they yield alcohol. When in solution they are decomposed at a boiling temperature, the solution, if neutral, becoming acid during the ebullition; but this change is prevented in the case of the sulphethylates of potash and soda, by the addition of a few drops of a solution of the hydrates of these alkalies.

Sulphethylate of potash is anhydrous and somewhat deliquescent, but insoluble in alcohol or ether. It crystallizes readily in large tables. *Sulphethylate of baryta* crystallizes with 2 Aq in rhombic prisms, which are soluble in water and in alcohol. *Sulphethylate of lime* ($CaO,C_4H_5O,S_2O_6+2\,Aq$) crystallizes in thin six-sided tables, very soluble in water but not in ether: it sometimes undergoes spontaneous decomposition. The neutral *sulphethylate of lead* ($PbO, C_4H_5O, S_2O_6+ 2\,Aq$) forms colourless tables, which are soluble in water and in alcohol; they also are liable to spontaneous decomposition. If digested upon an excess of oxide of lead, a soluble uncrystallizable subsalt, with 2 equivalents of base, is formed.

C_2HO_3) : or they may be produced by the action of a hydracid such as the hydrochloric, upon one of the alcohols ; hydrochlori ether (C_4H_5Cl) and hydriodic ether (C_4H_5I) affording examples this kind.

1. The *simple ethers* all contain oxygen, and are usuall formed by the distillation of the alcohol with sulphuric acid ; i this case the distilled liquid may be viewed as a compound deriv from an atom of alcohol by the removal of an atom of wate There are, however, reasons for thinking that the true relatio between the alcohol and the ether is of a different nature; bu supposing this hypothesis to be correct, the simple ethers migh be considered to consist of oxides of particular hydrocarbo (which form the radicles of the ethers), whilst the alcohols woul be hydrated oxides of the same bodies. Thus Liebig represen ordinary (ethylic) ether as oxide of ethyl (C_4H_5)O, and ordina alcohol as hydrated oxide of ethyl (C_4H_5)O,HO. Berzelius su gested, on the other hand, that ether and alcohol might each formed upon a similar plan, and later researches, particularly tho of Williamson, seem to have demonstrated that the molecular co stitution of alcohol is similar to that of ether ; so that both m be regarded as compounds formed upon the type of water $\left.\begin{matrix}H\\H\end{matrix}\right\}$ in which case alcohol would be water in which one-half of hydrogen has been displaced by ethyl ; and ether would be water which both halves of the hydrogen have been displaced by eth thus,

$$\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}}.$$

This doubling of the formula of ether has become ne sary in consequence of Williamson's discovery of the existe of double ethers, the general properties of which we proceed examine.

2. *Double* or *Mixed Ethers*.—When sodium or potassium added gradually to anhydrous alcohol, a brisk action occurs, temperature rises rapidly, and the metal is dissolved, whilst extrication of pure hydrogen gas takes place, and a fusible, tallizable, deliquescent compound is formed, which has recei the name of *sodium-alcohol* (or potassium-alcohol), or of *ethy of soda* (or of potash) ; its composition being such that it may regarded as alcohol in which its typical atom of hydrogen been displaced by an atom of sodium or of potassium (William *Q. J. Chem. Soc.*, iv. 106, 229) ; thus, if sodium be used :—

Ethionic anhydride . .	$C_4H_4\ 2\ S_2O_6$
Hydrated ethionic acid .	$2\ HO,C_4H_4\ 2\ S_2O_6$
Isethionic acid . . .	$HO,C_4H_5\ \ S_2O_7$

Consequently the change which occurs when hydrated ethionic acid is diluted with water and boiled, is the following:—

$$\overbrace{2\ HO,C_4H_4,2\ S_2O_6}^{\text{Hydrated Ethionic Acid.}}+H_2O_2=\overbrace{HO,C_4H_5S_2O_7}^{\text{Isethionic acid.}}+2\ \overbrace{HO,S_2O_6}^{\text{Sulphuric acid.}}.$$

Ethionic anhydride (C_4H_4, $2\ S_2O_6$) was termed by Magnus, its discoverer, *Sulphate of Carbyle.* It is prepared in the form of a white crystalline solid, by allowing the vapours of sulphuric anhydride to come into contact with dry olefiant gas in a bent tube kept cool. The same compound is obtained when a tube charged with anhydrous alcohol is placed in a bottle fitted with an accurately ground stopper, and containing sulphuric anhydride; in the course of a few days white silky crystals of ethionic anhydride are formed in the tube. These crystals melt at 176°, and deliquesce rapidly by exposure to the air. They are soluble in water and in alcohol with great elevation of temperature, and cannot be recovered by evaporating the liquid, for each atom of the compound assimilates 2 atoms of water, and becomes converted into the hydrated acid. The acid thus obtained, however, is not pure, since owing to the elevation of temperature a portion of ethionic is converted into isethionic acid. If the solution be neutralized by means of carbonate of baryta, and evaporated at a temperature below 212° until precipitation commences, ethionate of baryta is formed, and may be obtained by adding absolute alcohol until the density of the solution is reduced to 0·900; the salt thus precipitated is impure ethionate of baryta: it must be redissolved in water, and again precipitated by the addition of alcohol. The ethionates are soluble in water, but insoluble in alcohol; they are decomposed by a temperature of 212°. If ethionate of baryta be heated strongly in a tube, it yields sulphuric acid and a sublimate of sulphur, the residue containing sulphate of baryta and sulphide of barium. The ethionates of potash, ammonia, and soda may be readily obtained in crystals; they are prepared by decomposing a solution of ethionate of baryta by means of a solution of the respective sulphates of the different bases.

(988) *Other Vinic Acids.*—Sulpho-acids may be obtained from the methylic, tritylic, tetrylic, amylic, and other alcohols, by treating them in a manner similar to that directed for procuring

sulphethylic acid. Sulphomethylic acid may be obtained in crystals by evaporating its solution *in vacuo*. But the sulphuric is not the only acid which gives rise to these compound acids with the alcohols. The polybasic acids in general exhibit this power, even though their acid character may be but feeble. Carbonic, oxalic, and tartaric acids, for instance, may be made to yield compound acids analogous to the sulphethylic; and the same thing has been observed with sulphocarbonic acid (bisulphide of carbon). The tribasic acids, such as the phosphoric, even form two acid compounds. The formulæ of some of these coupled acids in the ethylic series and of their salts are exhibited in the following table:—

Vinic Acid.	Hydrate.	Metallic Salt.
Carbethylic . . .	HO,C_4H_5O,C_2O_4	KO,C_4H_5O,C_2O_4
Xanthic or sulphocarbethylic . .	HO,C_4H_5O,C_2S_4	KO,C_4H_5O,C_2S_4
Oxalethylic . . .	HO,C_4H_5O,C_4O_6	$KO.C_4H_5O,C_4O_6$
Tartrethylic . . .	$HO,C_4H_5O.C_8H_4O_{10}$	$KO,C_4H_5O,C_8H_4O_{10}$
Ethylsulphurous .	$HO.C_4H_5O,S_2O_4$	KO,C_4H_5O,S_2O_4
Phosphethylic . .	$2\,HO,C_4H_5O,PO_5$	$2\,BaO.C_4H_5O,PO_5 + 12\,Aq$
Diphosphethylic .	$HO, 2\,(C_4H_5O),PO_5$	$PbO, 2\,(C_4H_5O)\,PO_5$

Similar compounds may be formed with the other alcohols.

Carbethylic or *carbovinic acid* cannot be isolated, but the carbethylate of potash is obtained by transmitting a current of carbonic acid through a solution of hydrate of potash in absolute alcohol. It is soluble in alcohol, and forms pearly scales which are decomposed by water into bicarbonate of potash and alcohol.

Xanthic or *Sulphocarbethylic Acid.*—Xanthate or sulphocarbethylate of potash is a salt which crystallizes in needles. It is easily obtained by adding to an alcoholic solution of potash, a quantity of bisulphide of carbon, until the alkaline reaction has disappeared: on exposing the solution to a cold of 32°, the salt is deposited in needles; and the sulphocarbethylic acid may be obtained from this salt by decomposing a concentrated solution of it with hydrochloric acid, when it separates as a heavy oily liquid.

Oxalethylic Acid.—The oxalethylate (oxalovinate) of potash is obtained by decomposing oxalic ether dissolved in alcohol by a quantity of an alcoholic solution of potash sufficient to combine with one half of the oxalic acid which it contains. The alcoholic solution yields pearly scales of the salt, which, when decomposed with fluosilicic acid, furnishes free oxalethylic acid.

Ethylsulphurous or *sulphoethylolic acid* is obtained by acting upon mercaptan ($C_4H_6S_2$) (998) with nitric acid (of sp. gr. 1·23) so long as decomposition continues to take place: a violent reaction occurs, attended with the escape of nitrous fumes. The excess of nitric acid is expelled by evaporating the liquid over the water bath, and the residue, after dilution, is saturated with carbonate of lead; the filtered liquid is evaporated, and the ethylsulphite of lead is allowed to crystallize. If this salt be decomposed by means of sulphuretted hydrogen, the acid is set at liberty, and, by concentration over the water bath, it may be obtained in transparent crystals, which have an acid disagreeable taste.

Phosphethylic or *Phosphovinic Acid.*—When equal parts of alcohol and syrupy phosphoric acid are heated together, combination takes place; phosphethylate of baryta may be obtained by saturating the liquid with carbonate of baryta, distilling off the excess of alcohol and then filtering the solution and allowing it to crystallize. On decomposing this salt cautiously by the addition of sulphuric acid, the phosphethylic acid is liberated.

Diphosphethylic Acid.—By adding anhydrous phosphoric acid gradually to absolute alcohol, a mixture of phosphethylic and diphosphethylic acid is formed. On the addition of carbonate of lead, the phosphethylic acid and the excess of phosphoric acid are removed, whilst the diphosphethylate of lead remains in solution, and may be obtained in crystals by evaporation; if the acid be required in a separate form, it may be procured by passing sulphuretted hydrogen through a solution of the lead salt. When the diphosphethylate of lead is subjected to a heat of about 370°, it is decomposed, and phosphoric ether distils over:—

$$\overbrace{2\ [PbO,(C_4H_5O)_2,PO_5]}^{\text{Diphosphethylate of lead.}} = \overbrace{3\ C_4H_5O,PO_5}^{\text{Phosphoric ether.}} + \overbrace{2\ PbO,C_4H_5O,PO_5}^{\text{Phosphethylate of lead.}}.$$

§ III. The Ethers—Simple, Double, and Compound.

(989) *General Remarks on the Ethers.*—The ethers admit of being conveniently subdivided into three classes, viz., 1. The *simple ethers*, of which ordinary ether (C_4H_5O,C_4H_5O) is the best representative. 2. The *double* or *mixed ethers*, discovered by Williamson, such as the methyl-amylic ($C_2H_3O,C_{10}H_{11}O$), and the ethyl-octylic ($C_4H_5O,C_{16}H_{17}O$). 3. The *compound ethers*, which may either contain the elements of a simple ether and of an anhydrous oxy-acid, such as nitric ether (C_4H_5O,NO_5), acetate of amyl ($C_{10}H_{11}O,C_4H_3O_3$), and formiate of methyl (C_2H_3O,

C_2HO_3) : or they may be produced by the action of a hydracid, such as the hydrochloric, upon one of the alcohols ; hydrochloric ether (C_4H_5Cl) and hydriodic ether (C_4H_5I) affording examples of this kind.

1. The *simple ethers* all contain oxygen, and are usually formed by the distillation of the alcohol with sulphuric acid ; in this case the distilled liquid may be viewed as a compound derived from an atom of alcohol by the removal of an atom of water. There are, however, reasons for thinking that the true relation between the alcohol and the ether is of a different nature ; but, supposing this hypothesis to be correct, the simple ethers might be considered to consist of oxides of particular hydrocarbons (which form the radicles of the ethers), whilst the alcohols would be hydrated oxides of the same bodies. Thus Liebig represents ordinary (ethylic) ether as oxide of ethyl $(C_4H_5)O$, and ordinary alcohol as hydrated oxide of ethyl $(C_4H_5)O,HO$. Berzelius suggested, on the other hand, that ether and alcohol might each be formed upon a similar plan, and later researches, particularly those of Williamson, seem to have demonstrated that the molecular constitution of alcohol is similar to that of ether ; so that both may be regarded as compounds formed upon the type of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, in which case alcohol would be water in which one-half of the hydrogen has been displaced by ethyl ; and ether would be water in which both halves of the hydrogen have been displaced by ethyl ; thus,

$$\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}}.$$

This doubling of the formula of ether has become necessary in consequence of Williamson's discovery of the existence of double ethers, the general properties of which we proceed to examine.

2. *Double* or *Mixed Ethers.*—When sodium or potassium is added gradually to anhydrous alcohol, a brisk action occurs, the temperature rises rapidly, and the metal is dissolved, whilst an extrication of pure hydrogen gas takes place, and a fusible, crystallizable, deliquescent compound is formed, which has received the name of *sodium-alcohol* (or potassium-alcohol), or of *ethylate of soda* (or of potash) ; its composition being such that it may be regarded as alcohol in which its typical atom of hydrogen has been displaced by an atom of sodium or of potassium (Williamson *Q. J. Chem. Soc.*, iv. 106, 229) ; thus, if sodium be used :—

$$2\,\overbrace{(C_4H_5O,HO)}^{\text{Alcohol.}}+Na_2=2\,\overbrace{(C_4H_5O,NaO)}^{\text{Sodium alcohol.}}+H_2.$$

and the subsequent reactions may, perhaps, be more readily ed by throwing the equations into a form similar to the wing :—

$$2\,\overbrace{\left(\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2\right)}^{\text{Alcohol.}}+Na_2=2\,\overbrace{\left(\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2\right)}^{\text{Sodium-alcohol.}}+H_2.$$

action of sodium or potassium upon the other alcohols is of nalogous nature; for example, a similar result is obtained wood spirit is treated with sodium :—

$$2\,\overbrace{\left(\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O_2\right)}^{\text{Methyl alcohol.}}+Na_2\text{ becoming }2\,\overbrace{\left(\left.\begin{matrix}C_2H_3\\Na\end{matrix}\right\}O_2\right)}^{\text{Sodium methylalcohol.}}+H_2.$$

Now, if the sodium compound of alcohol be sealed up in a tube an equivalent amount of iodide of methyl, and heat be ed, mutual decomposition occurs; iodide of sodium being ed, whilst the methyl takes the place of the sodium in the ol, and thus a double or *mixed* ether, the ethyl-methylic, is ed :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2}^{\substack{\text{Sodium}\\\text{alcohol.}}}+\overbrace{\left.\begin{matrix}C_2H_3\\I\end{matrix}\right\}}^{\substack{\text{Iodide of}\\\text{methyl.}}}=\overbrace{\left.\begin{matrix}C_4H_5\\C_2H_3\end{matrix}\right\}O_2}^{\substack{\text{Ethyl-me-}\\\text{thylic ether.}}}+\overbrace{\left.\begin{matrix}Na\\I\end{matrix}\right\}}^{\substack{\text{Iodide of}\\\text{sodium.}}}$$

action of a similar kind is obtained if iodide of amyl be e to act upon the sodium-alcohol; amyl-ethylic ether being ed in this case, as follows :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2}^{\text{Sodium alcohol.}}+\overbrace{\left.\begin{matrix}C_{10}H_{11}\\I\end{matrix}\right\}}^{\text{Iodide of amyl.}}=\overbrace{\left.\begin{matrix}C_{10}H_{11}\\C_4\,H_5\end{matrix}\right\}O_2}^{\text{Amyl-ethylic ether.}}+\left.\begin{matrix}Na\\I\end{matrix}\right\}.$$

ral other double ethers have been formed by analogous hods. The uncombined molecule of each of these ethers yields lumes of vapour, as may be seen by comparing the theoretical the experimental numbers :—

Double ether.	Formula.	Boiling Point ° F.	Specific Gravity.	
			Theory.	Experiment
thyl-ethylic ether . . .	$C_2H_3O,C_4\,H_5\,O$	51·8	2·084	2·158
thyl-amylic ether . . .	$C_2H_3O,C_{10}H_{11}O$	197·6	3·546	3·74
yl-ethylic ether . . .	$C_4H_5O,C_{10}H_{11}O$	233·6	4·031	4·042

It is certain that these bodies are truly compounds, and not mere mixtures of the two ethers; the constancy of their boiling points alone would be sufficient to prove this fact: for example, methylic ether is gaseous at ordinary temperatures, and ethylic ether boils at $94^{\circ}\cdot8$, but the compound ether has a fixed boiling point at $51^{\circ}\cdot8$.

Now, if iodide of ethyl be substituted for the iodide of amyl, or iodide of methyl, in the foregoing experiment, the iodide of ethyl also is decomposed by the sodium-alcohol, and ordinary ether is produced:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2}^{\text{Sodium alcohol.}} + \overbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}^{\text{Iodide of ethyl.}} = \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ethylic ether.}} + \overbrace{\left.\begin{matrix}Na\\I\end{matrix}\right\}}^{\text{Iodide of sodium.}}.$$

The conclusion, therefore, appears to be inevitable, that the molecule of common ether must likewise be analogous in its construction to the molecules of the double ethers. Moreover, if the uncombined molecule of ether be regarded as composed only of C_4H_5O, it yields only two volumes of vapour; whereas, if the molecule be taken as (C_4H_5O,C_4H_5O), it yields four volumes of vapour, like alcohol and the other organic compounds.

3. *Compound Ethers.*—When one of the alcohols is brought into contact with a hydrated monobasic acid, the two bodies react upon each other, in the proportion of one equivalent of each, two equivalents of water are eliminated, and the elements of the anhydrous acid and of the ether unite together, and form a compound ether. Thus, when acetic acid is subjected to distillation with ordinary alcohol, acetic ether is produced:—

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2}^{\text{Acetic acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} = \overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_5\end{matrix}\right\}O_2}^{\text{Acetic ether.}} + \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}}$$

A double decomposition occurs in this case, as in the foregoing, the basic hydrogen of the acetic acid changing places with the ethyl contained in the alcohol. When the affinities of the acid are not very strong, the reaction is facilitated by mixing one of the salts of the acid with alcohol, and then liberating the acid by the agency of sulphuric acid; in this manner formic ether is readily obtained by distilling a mixture of dry formiate of soda, alcohol, and concentrated sulphuric acid, although hydrated formic acid and alcohol, when distilled together, have but a comparatively small action upon each other. Berthelot found that by exposing the alcohol and the acid in sealed tubes for some a temperature varying from 212° to 480°, the reaction of ic acid upon the alcohol might in most cases be obtained he intervention of a stronger acid.

y compound ethers, such as the butyric, the benzoic, and itic, may, according to Berthelot (*Ann. de Chimie*, III.), be obtained by sealing up a mixture of the hydrated the simple oxygen ether in a tube, and exposing it to a ure of about 750°: much of the ether remains unconverted, great the excess of acid employed. In this case water compound ether are the sole products, no alcohol being contrary to what might have been expected, one atom of HO) being separated from each atom of hydrated acid:—

$$\left.\right\}O_2 + 2\left(\overbrace{\left.\begin{matrix}C_{32}H_{31}O_2\\ H\end{matrix}\right\}O_2}^{\text{Palmitic acid.}}\right) = \overbrace{\left.\begin{matrix}H\\ H\end{matrix}\right\}O_2}^{\text{Water.}} + 2\left(\overbrace{\left.\begin{matrix}C_{32}H_{31}O_2\\ C_4H_5\end{matrix}\right\}O_2}^{\text{Palmitic ether.}}\right)$$

er modes may be adopted for obtaining the compound When the oxychlorides of the monobasic acids (1094) ted with alcohol, a compound ether of the corresponding sic acid is obtained: thus benzoic oxychloride (chloride zoyl) yields benzoic ether when heated with anhydrous :—

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\ Cl\end{matrix}\right\}}^{\text{Benzoic oxychlor.}} + \overbrace{\left.\begin{matrix}C_4H_5\\ H\end{matrix}\right\}O_2}^{\text{Alcohol.}} = \overbrace{\left.\begin{matrix}H\\ Cl\end{matrix}\right\}}^{\text{Hydrochloric acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\ C_{14}H_5O_2\end{matrix}\right\}O_2}^{\text{Benzoic ether.}}.$$

distillation of the concentrated aqueous solution of a lt, such as the sulphomethylate or sulphethylate of potash ne, with a concentrated solution of the sulphide, selenide, , or cyanide of potassium, furnishes an easy method of g the corresponding ether with sulphur, selenium, tellu- cyanogen. Thus if the cyanide of methyl were required, tion would be the following:—

$$KCy + \overbrace{KO,C_2H_3O,S_2O_6}^{\text{Sulphomethylate of potash.}} = \overbrace{C_2H_3Cy}^{\text{Cyanide of methyl.}} + \overbrace{2\ KO,S_2O_6}^{\text{Sulphate of potash.}}.$$

er modes of preparing particular ethers are adopted; ill be noticed when the ethers to which they apply are d.

ethers of the hydracids are readily formed by the direct f these acids upon the alcohols; hydrochloric ether, for , may be formed by saturating alcohol with hydrochloric , and submitting the mixture to *distillation*:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}^{\text{Alcohol.}}O_2+\overbrace{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}^{\text{Hydrochloric acid.}}=\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}}^{\text{Water.}}O_2+\overbrace{\left.\begin{matrix}C_4H_5\\Cl\end{matrix}\right\}}^{\text{Hydrochloric ether.}}$$

The atom of ethyl in the alcohol, and that of hydrogen in the acid, change places, and hydrochloric ether and water are produced by double decomposition.

Advantage is taken of the facility with which the hydracids act upon the alcohols, in order to prepare compound ethers with acids of comparatively feeble affinities. Thus if it be desired to obtain ethers of the fatty acids, such as palmitic ether for example, the palmitic acid is dissolved in alcohol, and a current of hydrochloric acid is transmitted, whilst the alcohol is gently heated. After the reaction has terminated, the product is washed with hot water; and the palmitic ether being insoluble in water, is readily separated from the mixture. It appears that hydrochloric ether is first formed, and this afterwards undergoes double decomposition when heated with the fatty acid:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\Cl\end{matrix}\right\}}^{\text{Hydrochloric ether.}}+\overbrace{\left.\begin{matrix}C_{32}H_{31}O_2\\H\end{matrix}\right\}O_2}^{\text{Palmitic acid.}}=\left.\begin{matrix}H\\Cl\end{matrix}\right\}+\overbrace{\left.\begin{matrix}C_{32}H_{31}O_2\\C_4H_5\end{matrix}\right\}O_2}^{\text{Palmitic ether.}}.$$

The ethers of the dibasic acids, when converted into vapour, yield only 2 volumes of vapour for each atom of oxide of ethyl (C_4H_5O) which they contain: so that if 4 volumes of vapour be taken as the representative of the uncombined molecule of those compounds, the molecular formula of the oxalic, carbonic, and succinic ethers must be taken as containing one atom of the dibasic acid and 2 atoms of oxide of ethyl; the formula of carbonic ether being written ($2\,C_4H_5O,C_2O_4$).

(990) *Nature of the Compound Ethers.*—Liebig proposed to consider the compound ethers as salts, in which the acid is supposed to be combined with an organic oxide instead of a metallic one; acetic ether, for example, being regarded as acetate of oxide of ethyl; $(C_4H_5)O,C_4H_3O_3$. The organic oxide, however, cannot readily be displaced by a metallic oxide,—as oxide of ammonium can from its salts, by means of oxide of potassium; and the properties of ethers, as well as the mode of their formation, are in reality more allied to those of the amides than to the ordinary salts. Indeed, they present a striking analogy with the amides (1164), as may be seen on comparing them in a few leading particulars.

The amides are formed by the union of ammonia with the whilst an elimination of water takes place. Benzamide, for ce, consists of the elements of single atoms of benzoic acid and nia, minus 2 atoms of water; thus—

$$\overbrace{\left.\begin{matrix}H\\H\\H\end{matrix}\right\}}^{\text{Ammonia.}}N+\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}}^{\text{Benzoic acid.}}O_2=\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\\H\end{matrix}\right\}}^{\text{Benzamide.}}N+\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}}^{\text{Water.}}O_2.$$

ic ether contains the elements of single atoms of benzoic nd alcohol, also minus two atoms of water:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}^{\text{Alcohol.}}O_2+\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}}^{\text{Benzoic acid.}}O_2=\left.\begin{matrix}H\\H\end{matrix}\right\}O_2+\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\C_4H_5\end{matrix}\right\}}^{\text{Benzoic ether.}}O_2.$$

mides, when treated with hydrating agents, as, for instance, boiled with alkalies, slowly become hydrated, whilst ammonia, e acid from which they were formed, are reproduced: and manner the compound ethers, when treated with a solution ash, are resolved into alcohol, and the acid from which they formed. Indeed, this change of the compound ethers into l and the hydrated acid often takes place by mere prolonged t with water, and this decomposition is greatly accelerated presence of a small quantity of free acid, particularly if the rature be raised to the boiling point. When heated with under pressure, the compound ethers, as a rule, become con- into free hydrated acid and the alcohol of the ether iwetz).

gain, the dibasic acids form with amidogen, *amidic* acids, may be regarded as acids in which one half of the acid has enced a reduction to the form of amide by the action of 1 of ammonia; and the vinic acids, in like manner, may be d as dibasic acids in which one half the acid has been con- d into a compound ether by the action of 1 atom of one of lcohols. Oxamic and oxalethylic (oxalovinic) acids, for in- e, may be represented respectively as compounds of oxalic with oxamide and with oxalic ether:—

$$\overbrace{H_4N_2C_4O_4}^{\text{Oxamide.}}+\overbrace{2\ HO,C_4O_6}^{\text{Oxalic acid.}}=\overbrace{2\ HO,H_4N_2C_4O_4,C_4O_6}^{\text{2 eqs. Oxamic acid.}}.$$

$$2\,\overbrace{C_4H_5O,C_4O_6}^{\text{Oxalic ether.}}+2\,\overbrace{HO,C_4O_6}^{\text{Oxalic acid.}}=\overbrace{2\,(HO,C_4H_5O,C_4O_6)}^{\text{2 eqs. Oxalethylic acid.}}.$$

91) *Chemical Properties of the Ethers.*—The simple ethers,

and the compound ethers of the monobasic acids, may gen
volatilized without undergoing decomposition; but their
point rises about 39° for each additional equivalent of th
carbon (C_2H_2). A similar observation may be applied
boiling point of compound ethers of different alcohols deri
the same acid, as well as to that of ethers derived from the sa
hol but containing different but homologous acids. The et
generally sparingly soluble in water, but they are readily d
by alcohol and by ordinary ether. None of the simple
have as yet been detected ready formed in the vegetable ki
but the compound ethers appear to be not unfrequently pr
fruits and some other parts of plants, which occasionally o
fragrance to these bodies. The *oil of winter green* is a sa
of methyl ($C_2H_3O,C_{14}H_5O_5$), and, as Cahours has shown,
be artificially produced by the combination of oxide of
with salicylic acid. Many of the artificial essences sold
perfumers and confectioners consist of compound ethers diss
alcohol; for it is a remarkable circumstance, that the pur
often have a repulsive odour, which is very different from th
they possess when largely diluted with alcohol. The s
pear oil, or *essence of Jargonelle pear*, is an alcoholic sol
acetate of amyl, $C_{10}H_{11}O,C_4H_3O_3$. *Apple oil* is a similar p
tion of valerianate of amyl, $C_{10}H_{11}O,C_{10}H_9O_3$. *Pine-appl*
simply butyric ether ($C_4H_5O, C_8H_7O_3$) diluted with alcoho
mann, *Ann. de Chimie*, III. xxxiv. 325). *Essence of melons* is t
compound of one of the acids of cocoa-nut oil. *Essence of q*
dilute pelargonic ether, $C_4H_5O, C_{18}H_{17}O_3$; and the peculia
of wine is found to be due to an ether, termed by Lie
Pelouze, who discovered it, *œnanthic ether* (from οἶνος, wi
which, according to Delffs, is the same as pelargoni
$C_4H_5O, C_{18}H_{17}O_3$. This ether is stated to be the basis of *Hu*
wine oil, which has been sold at a very high price for fla
brandy.

(*a*) *Ordinary Ether—Theory of Etherification.*

(992) ETHER; *Ethylic* or *Vinic Ether*, sometimes imp
called *Sulphuric Ether* $(C_4H_5,O)_2=74$: *Sp. gr. of liquid*
0·7365; *of vapour* 2·586; *Boiling pt.* 94°·8.

Preparation.—Formerly ether was prepared by mixing
sures of alcohol and 1 measure of sulphuric acid, and di
until it began to blacken; then a quantity of alcohol, e
half that originally used, was added to the residue in the
and the distillation was again proceeded with until the ether

to come over. The method at present in general use for the preparation of ether is that known as the 'continuous process' of Boullay. It consists in mixing together equal measures of alcohol (sp. gr. 0·830), and concentrated sulphuric acid; the mixture is submitted to distillation in a capacious retort, which must be connected with an efficient condenser. Through the tubulure of the retort a tube is introduced, which is in communication with a reservoir of alcohol, designed to maintain a supply of spirit sufficient to keep the amount of liquid at a uniform level in the retort during the course of the subsequent distillation. The temperature is then rapidly raised so as to maintain the mixture in steady ebullition. The liquid which passes over consists almost entirely of ether and water, mixed with a small portion of alcohol, which has distilled over unchanged.

This process may go on without interruption until a quantity of alcohol, about 30 times as great as that originally taken, has become converted into ether. Isethionic acid is gradually formed in the residue.

Mitscherlich distilled a mixture of 1 part of absolute alcohol with 2 parts of sulphuric acid, consisting of 5 parts of oil of vitriol diluted with 1 part of water ($2\,HO,S_2O_6,+2\,HO$; sp.gr. 1·78 nearly), the original volume of liquid in the retort being maintained by a gradual supply of absolute alcohol; he found that for every 100 parts of alcohol consumed, about 65 of ether, 17 of water, and 18 of undecomposed alcohol were obtained: the quantity of alcohol which distils depending upon the rapidity with which the operation is conducted; the more quickly it is performed the larger being the quantity of alcohol. When absolute alcohol is used, for every 65 parts of ether obtained, 15·4 of water should be produced, the slight excess observed depending upon the presence of traces of water in the alcohol. With a more dilute alcohol the proportion of water which passes over is greater, the excess corresponding with the amount present in the alcohol. The temperature most favourable to the formation of ether is from 284° to 290°. At a temperature of 320° the disengagement of sulphurous acid mixed with olefiant gas and oil of wine commences. If a sulphuric acid much more dilute than one of sp. gr. 1·632 ($2\,HO,S_2O_6,+4\,HO$) be employed, the excess of water gradually distils over with the alcohol, which undergoes little change until the liquid has become sufficiently concentrated to allow the boiling point to rise to 284°, after which ether is formed as usual. Alcohol may also be converted into ether by heating it with phosphoric, arsenic, and perchloric acids, as well as by means of bichloride of tin, chloride of zinc, fluoride of boron, and by several other processes which will be further considered when the theory of etherification is passed under review (993).

In order to purify the crude ether, it should be agitated with an equal bulk of water, containing $\frac{1}{16}$th of its weight of carbonate of potash in solution; the water combines with the alcohol, and the potash unites with any sulphurous acid that may have distilled over: the liquid separates into two layers, the upper part of which consists of ether holding a little water in solution. The ether may be freed from water by allowing it to stand for a day or two upon quicklime, or upon chloride of calcium: it is then to be rectified by the heat of a water-bath, and condensed in vessels kept cool with ice-cold water.

Properties.—Pure ether is a very limpid, colourless, transparent, volatile liquid, of high refracting power; it possesses a powerful, penetrating, and peculiar odour, and a taste at first fiery, but afterwards cooling: if taken internally it produces stimulating and intoxicating effects. Its vapour, when inhaled, at first occasions exhilaration, speedily followed by complete insensibility to pain; owing to this property it was at one time extensively administered during surgical operations, to diminish the sufferings of the patient; but its employment for this purpose has been superseded by the use of chloroform, the effects of which are more speedy and certain, and are attended with less excitement to the system. Ether has a sp. gr. of 0·724 at 55°; and it is usually stated to freeze at $-24°$. It is probable, however, that the specimen which gave this result was not pure, as according to Mitchell, it may be exposed to a cold of $-146°$ without becoming solid. From its great volatility, and the consequent depression of temperature furnished by its rapid evaporation, it is frequently employed for producing cold artificially. Ether is dissolved freely by alcohol, but sparingly by water. When agitated with an equal bulk of water, it dissolves about $\frac{1}{30}$th of its volume of water, while the water takes $\frac{1}{8}$th of its bulk of ether. Ether is employed to some extent as a solvent for fatty bodies, and is used in the proximate analysis of organic matters for separating the fats or oils which they contain, from other substances which are not soluble in ether. Iodine, sulphur, and phosphorus are dissolved by ether. Ammoniacal gas, and deutoxide of nitrogen, are also freely absorbed by it: certain metallic salts are likewise dissolved by it; among these are bichloride of platinum, and sesquichloride of iron: with bichloride of tin it forms a volatile crystalline compound $(C_4H_5O)_2\ SnCl_2$; and a similar compound containing titanium may likewise be procured. Chloride of mercury and terchloride of gold are also freely soluble in ether; these two compounds may be separated from their solutions in water by agitation with ether, and they rise with it to the surface when left at rest.

Ether is highly inflammable, and as it is also very volatile and furnishes a vapour of considerable density, care must be taken not to pour it out in the vicinity of a flame; many serious accidents having arisen from a neglect of this precaution. In certain proportions its vapour forms an explosive mixture with air or oxygen. When burned with a sufficient supply of oxygen it produces only water and carbonic acid. Its flame is more luminous than that of alcohol, and it deposits charcoal on cold bodies which are introduced into it. When passed through ignited porcelain tubes filled with fragments of porcelain it is decomposed; charcoal is deposited, and aldehyd is found among the products. If the temperature be not too high, a large quantity of acetylene (C_4H_2) (1043) is obtained, mixed with olefiant gas. If burned at a lower heat with insufficient access of air, it yields a mixture of aldehyd with acetic acid and acetal; but aldehyd is the predominating ingredient: this formation of aldehyd is easily explained, since the substitution of two atoms of oxygen for two of hydrogen in the formula for ether, furnishes the elements of two atoms of aldehyd, the hydrogen combining with two more atoms of oxygen, and being eliminated in the form of water:—

$$\overbrace{C_4H_5O)_2}^{\text{Ether.}} + O_4 = 2\ (\overbrace{C_4H_4O_2}^{\text{Aldehyd.}}) + H_2O_2.$$

If ether be kept in vessels partially filled with air, it gradually absorbs oxygen, and acetic acid is formed. When treated with concentrated sulphuric acid, ordinary ether becomes converted into sulphethylic acid; and if this liquid be boiled, sweet oil of wine mingled with sulphurous acid passes over; the mixture blackens considerably, and ethionic and isethionic acids are formed in the retort.

Nitric acid acts powerfully upon ether with the aid of heat, forming carbonic, acetic, and oxalic acids.

If ether be saturated with hydrochloric acid and distilled, hydrochloric ether is the product, and the effects of hydrobromic and hydriodic acid are analogous, though the bromide and iodide of ethyl are less easily produced. Chlorine converts ether into various substitution compounds (1018), and produces aldehyd, chloral, and hydrochloric ether, whilst hydrochloric acid is evolved in abundance.

Potassium and sodium decompose ether slowly, and liberate hydrogen gas.

(993) *Theory of Etherification.*—In the process of preparing ether from alcohol by the agency of sulphuric acid, it will be observed that a small quantity of this acid converts an indefinite quantity of alcohol into ether and water. The explanations which have been offered to account for the formation of ether by the action of sulphuric acid are very numerous. Most chemists, however, now admit with Liebig, that the essential change may be divided into two stages, the first of which consists in the formation of sulphethylic acid, and the second in the decomposition of this acid into sulphuric acid, water, and ether. When fresh alcohol is added to the mixture, a new quantity of sulphethylic acid is formed with the sulphuric acid liberated during the previous distillation; this sulphethylic acid in its turn undergoes decomposition into ether, water, and sulphuric acid, and thus the same portion of sulphuric acid continues the etherification for an indefinite period. The following ingenious experiment by Williamson goes far towards proving the occurrence of this successive formation and decomposition of sulphethylic acid during the process of etherification. A mixture of sulphuric acid and amylic alcohol was prepared, so as to obtain sulphamylic acid ($HO,C_{10}H_{11}O,S_2O_6$) (one of the homologues of sulphethylic acid); this mixture was placed in a retort and then submitted to distillation, supplying it with ordinary alcohol, as in the continuous process of making ether already described. The distillation was continued until the liquid which passed over contained only ordinary ether, without any compound of fousel oil. On examining the residue in the retort it was found to contain sulphethylic acid only, the sulphamylic acid having entirely disappeared, a double ether (amylethylic ether, $C_4H_5O,C_{10}H_{11}O$) being found in the first portions of the distilled liquid. The successive stages of this action may be traced as follows:—

$$(1)\ \overbrace{\left.\begin{matrix}C_{10}H_{11}\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphamylic acid.}}+\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{1st atom alcohol.}}=\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphuric acid.}}+\overbrace{\left.\begin{matrix}C_4H_5\\C_{10}H_{11}\end{matrix}\right\}O_2}^{\text{Amylethylic ether,}}.$$

$$(2)\ \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphuric acid.}}+\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{2nd atom alcohol.}}=\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphovinic acid.}}+\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}}.$$

$$(3)\ \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphovinic acid.}}+\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{3rd atom alcohol.}}=\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphuric acid.}}+\overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}}.$$

Now, since two successive stages have been proved to occur during the formation of this double ether, and since they have been also traced with other double ethers, it appears to be highly probable that similar steps attend the formation of common ether by the continuous process, in which it may be supposed that the first reaction takes place between one double equivalent of sulphuric acid and an equivalent of alcohol; one of the atoms of basic hydrogen in the acid exchanging places with the ethyl of the alcohol, thus forming one atom of sulphethylic acid and a double molecule of water, as follows:—

$$\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphuric acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} = \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphethylic acid.}} + \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}};$$

but in the second stage of the reaction, the newly-formed sulphethylic acid, and a new atom of alcohol undergo double decomposition, the basic hydrogen of the alcohol being substituted for the atom of ethyl contained in the sulphethylic acid; a molecule of ether being produced, whilst the double equivalent of sulphuric acid is again set at liberty to perform a similar round with fresh portions of alcohol:—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphethylic acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{2nd atom alcohol.}} = \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2,S_2O_6}^{\text{Sulphuric acid.}} + \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}}.$$

The principal difficulty in admitting this view arises from the paradoxical circumstance, that the sulphethylic acid should be produced and decomposed under precisely similar circumstances of temperature. Mitscherlich, Berzelius, and Graham therefore assume that sulphuric acid has the power of producing a decomposition of alcohol into ether and water, by some unexplained action, to which the terms contact-action and catalytic force have been applied. (859 *et seq.*) Mitscherlich even considers the formation of sulphethylic acid as an accidental circumstance not connected with the formation of ether. The following is one of the experiments upon which he relies in support of this view:— A mixture of sulphuric acid and water was prepared of such a strength that it boiled at 290° (sp. gr. 1·52), and the vapour of boiling alcohol was transmitted into it whilst the acid was kept at the boiling point. After the alcohol vapours had been transmitted for a short interval, ether and water began to collect in the receiver, and continued to do so as long as the current of vapour was kept up, four-fifths of the alcohol undergoing decomposition, about one-fifth only passing over unchanged, and this portion probably escaped simply because, from the rapidity of the current vapour, it did not come completely into contact with the ac Now, it is argued that, from the evolution of latent heat whi accompanies the condensation of vapour, the points in which th alcohol vapour were condensed by the acid must have been con siderably above 290°; but as sulphethylic acid is decompos below this temperature, it appears to be impossible, that und these circumstances any of this acid could have been formed, an subsequently decomposed. If the dilution of the acid were le considerable (sp. gr. 1·61), and only sufficient to reduce the boili point to 325° or 330°, the alcohol vapour when transmitted throu the boiling liquid was converted into olefiant gas and water (39 (C_4H_5O,HO) becoming $C_4H_4+H_2O_2$; scarcely any ether be evolved during the reaction, and no deposit of carbon occurrin It would be difficult to resist the inference of Mitscherlich if th vapours of the alcohol underwent *immediate* decomposition contact with the boiling acid, but it is important to observe th this is not the case, as is at once evident on repeating the t experiments. It is not until a certain quantity of alcohol has be condensed in the acid, that the formation of ether, or of olefia gas, begins; consequently the mixture is in circumstances sembling those under which ether is habitually produced.

Graham has also made some experiments which throw so doubt upon the necessity of the successive formation and deco position of sulphethylic acid in the preparation of ether (Q. *Chem. Soc.*, iii. 24). In these experiments, mixtures of alco and sulphuric acid, in different proportions, were enclosed in se tubes, and subjected for an hour to a temperature ranging fr 284° to 352°. It was found that when 1 volume of oil of vi was added slowly to 4 volumes of alcohol (sp. gr. 0·841), th sealed up and heated, the liquid separated into two layers; upper one occupied one-third of the bulk of the whole liquid, was nearly pure ether; the lower layer contained a mixture water, alcohol, and sulphuric acid, but scarcely any sulpheth acid; the lower stratum of the liquid had a slight yellow ti but the upper layer was colourless. When 8 measures of alco were mixed with 1 of acid, the proportion of ether which flo was still equal to one-third of the bulk of the entire liquid. the other hand, when the formation of sulphethylic acid favoured by reducing the proportion of alcohol, the production ether became insignificant. Thus, when the quantity of alc only amounted to twice the bulk of the acid, the liquid assu [illegible] brown colour after heating, and only a film of e el on standing; and when equal volumes of acid and alcohol ed, a black, opaque, gummy liquid was formed without any ible stratum of ether.

en glacial phosphoric acid, and when biphosphate of soda bstituted for sulphuric acid, no ether was formed even the mixture was heated to 360°. Chloride of zinc, under circumstances, produced only traces of ether. But when ized bisulphate of soda containing a slight excess of acid ployed, it was found to etherize twice its bulk of alcohol tually as free sulphuric acid.

till more striking experiment was made by taking a portion rdinary ether mixture, viz., 100 parts of oil of vitriol, 48 of (sp. gr. 0·841), and 18·5 of water, placing it in a sealed nd heating for an hour to 290°. Sulphethylic acid was d, but no ether was formed. It was then divided into two , to one of which half its bulk of alcohol was added, to the alf its bulk of water; the two were sealed up in separate nd again heated. No ether was formed in the tube to ater was added, while in the other, the formation of ether siderable. Hence it appears that the sulphethylic acid in ular state of dilution is resolved into alcohol and diluted ic acid, but when mixed with alcohol it is decomposed into d sulphuric acid; and the latter when liberated acts upon portion of alcohol and reproduces sulphethylic acid.

ohol, even when mixed with very small proportions of sulph- acid, was found by Reynoso to be etherized by prolonged under pressure; the more diluted the acid the higher was perature and the longer the time required. Reynoso e *Chimie*, III. xlviii. 390) finds that the hydrochloric, omic, and hydriodic acids act similarly when heated for hours to 460° in sealed tubes with an excess of alcohol.

ous salts are also capable of etherifying alcohol, if heated y with it under pressure. Reynoso states, that the crystallized neutral sulphates, isomorphous with sulphate esia, when sealed up with alcohol in tubes and heated to effect a partial etherification of the alcohol: whilst the s themselves, with the exception of those of nickel and experience no change beyond the loss of their water of zation. Tersulphate of alumina etherizes alcohol between d 460° with but little formation of basic sulphate of the nd without any liberation of gas; when alum is used the are similar, but the alcohol is etherified at a lower tempe- Both iodide and bromide of cadmium, and the chlorides

of cobalt, cadmium, manganese, and copper, under similar c
stances effect the etherification of alcohol, but undergo no
themselves. With protochlorides of tin and of copper, the
tion of ether is sufficient to furnish a considerable stratum of
but a certain amount of permanent gas is also formed. C
of mercury blackens the alcohol, ether is formed, and mu
is liberated. Chlorides of zinc and ammonium effect a
change; the chlorides of aluminum, antimony, and perchlo
iron yield a mixture of ether and hydrochloric ether.

Chloride of ethyl, as well as bromide and iodide of ethyl
heated with an excess of alcohol in sealed tubes to 390°
hours, converts the alcohol into a mixture of ether and
whilst hydrochloric, hydrobromic, or hydriodic acid is lib
Probably the action, as Reynoso suggests, consists in the suc
formation of hydrochloric, hydrobromic, or hydriodic acid, a
conversion of the acid into chloride, bromide, or iodide o
with liberation of water, in which case the reaction with b
of ethyl might be represented as follows:—

$$\overbrace{\left.\begin{array}{r}C_4H_5\\H\end{array}\right\}O_2}^{\text{Alcohol.}}+\overbrace{\left.\begin{array}{r}C_4H_5\\Br\end{array}\right\}}^{\text{Brom. ethyl.}}=\overbrace{\left.\begin{array}{r}C_4H_5\\C_4H_5\end{array}\right\}O_2}^{\text{Ether.}}+\left.\begin{array}{r}H\\Br\end{array}\right\}$$

and again:—

$$\left.\begin{array}{r}C_4H_5\\H\end{array}\right\}O_2+\left.\begin{array}{r}H\\Br\end{array}\right\}=\left.\begin{array}{r}H\\H\end{array}\right\}O_2+\left.\begin{array}{r}C_4H_5\\Br\end{array}\right\}$$

The hydrobromic ether thus formed going through the sam
of changes with successive portions of alcohol.

It is obvious that the metallic chlorides act in some
as yet unexplained, upon the alcohol, in consequence of wh
latter becomes more or less completely resolved into eth
water. This effect cannot be produced by the action o
alone; and it must be admitted, that the theory of etheri
is still incomplete, notwithstanding the numerous resear
which it has been the subject.

The oxygen in ordinary ether may be displaced by other
analogous to it, such as sulphur, selenium, and tellurium,
as by chlorine, bromine, and iodine. The compounds thus
are sometimes described under the names of hydrosulphuric,
chloric, hydrobromic, and hydriodic ethers.

(994) The following table exhibits the composition of a fe
principal compound ethylic ethers. It would be useless to
to enumerate them all, since every acid forms at least one
and some, such as the silicic and boracic, furnish more tha
(the densities to which an asterisk is affixed were taken at 32

Ethylic Ethers.

e of Ether.	Formulæ (= 4 Vols. Vapour.)	Boiling Point ° F.	Specific Gravity.	
			Liquid.	Vapour.
ethyl	$(C_4H_5O)_2$	94·8	0·7365*	2·586
. . . . .	$(C_4H_5S)_2$	163·4	0·825	3·1
lo	$(C_4H_5S_2)_2$	304·0	1·0	4·27
. . . . .	C_4H_5Cl	51·9	0·921*	2·219
. . . . .	C_4H_5Br	105·8	1·4733*	3·754
. . . . .	C_4H_5I	158·5	1·9755*	5·475
. . . . .	C_4H_5,C_2N	190	0·787	
. . . . .	$2\ C_4H_5O,S_2O_6$		1·120	
. . . . .	$2\ C_4H_5O,S_2O_4$	320	1·1063*	4·78
. . . . .	C_4H_5O,NO_5	185	1·112	
. . . . .	C_4H_5O,NO_3	62	0·947	2·627
e	$3\ C_4H_5O,PO_5$		1·086	
e	$2\ C_4H_5O,C_2O_4$	257	0·975	4·09
. . . . .	$3\ C_4H_5O,BO_3$	246	0·8849*	5·31
).	$(2\ C_4H_5O,SiO_2)_2$	330	0·933	7·32
. . . . .	C_4H_5O,SiO_2	662	1·079	
. . . . .	C_4H_5O,C_2HO_3	127·7	0·9357*	2·573
. . . . .	$C_4H_5O,C_4H_3O_3$	164·9	0·9069*	3·067
. . . . .	$C_4H_5O,C_8H_7O_3$	238·8	0·9041*	4·04
. . . . .	$C_4H_5O,C_{10}H_9O_3$	272·3	0·894	4·558
. . . . .	C_4H_5O,C_2NO	140	0·8981	2·475
e	$3\ C_4H_5O,C_6N_3O_3$	487		7·4
. . . . .	$C_4H_5O,C_{14}H_5O_3$	408·2	1·053	5·407
. . . . .	$C_4H_5O,C_6H_5O_5$		1·08	4·75
. . . . .	$2\ C_4H_5O,C_4O_6$	363·2	1·0929	5·087
. . . . .	$2\ C_4H_5O,C_8H_4O_6$	417·0	1·036	6·22
. . . . .	$3\ C_4H_5O,C_{12}H_5O_{11}$	541·4	1·142	

(*b*) *Hydracid Ethylic Ethers.*

Hydrochloric Ether ; or *Chloride of Ethyl* (C_4H_5Cl) : *vapour* 2·219 ; *of liquid* at 32°, 0·921 ; *Boiling pt.* 51°·9 ompound is obtained easily either by saturating alcohol ochloric acid gas, and then distilling at a gentle heat, or g a mixture of 3 parts of oil of vitriol, 2 of alcohol, and d chloride of sodium ; the retort is in either case conth a tubulated receiver surrounded by water at a temf about 70°, where most of the alcohol and water which during the operation are condensed, while the ether the form of vapour through a bent tube which is in the tubulure of the receiver, and passes to the bottom kept cool with ice. The liquid which is condensed in must be rectified from chloride of calcium :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}^{\text{Alcohol.}}O_2+\left.\begin{matrix}H\\Cl\end{matrix}\right\}=\left.\begin{matrix}H\\H\end{matrix}\right\}O_2+\overbrace{\left.\begin{matrix}C_4H_5\\Cl\end{matrix}\right\}}^{\text{Chloride ethyl.}}.$$

Another mode in which it may be formed consists in heating anhydrous ether with terchloride of phosphorus to 380° in a sealed tube, chloride of ethyl and phosphorous acid being formed, 3 molecules of ether reacting upon 2 of the terchloride:—

$$3\left(\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2\right)+2\,PCl_3=6\,C_4H_5Cl+2\,PO_3.$$

Chloride of ethyl is also formed by the action of other chlorides, such as chloride of sulphur, antimony, tin, or zinc, upon alcohol. Chloride of ethyl is a colourless liquid, of a penetrating, ethereal, and somewhat alliaceous odour. It is slightly soluble in water, and burns with a brilliant flame edged with green, emitting fumes of hydrochloric acid. If passed through red-hot tubes, it is decomposed into equal measures of hydrochloric acid and olefiant gas ; $C_4H_5Cl=C_4H_4+HCl$. It is sparingly soluble in water, but is freely dissolved by alcohol. These solutions give no precipitate with nitrate of silver. If an alcoholic solution of potash be enclosed in a sealed tube with hydrochloric ether and heated to 212°, chloride of potassium and ordinary ether are formed; $2\ C_4H_5Cl+2\ (KO,HO) = (C_4H_5O)_2+2\ KCl+H_2O_2$ (Balard); but if the vapour of the ether be passed over heated hydrate of potash, water and pure olefiant gas are evolved; $C_4H_5Cl+KO,HO=C_4H_4+H_2O_2+KCl$.

(996) *Hydrobromic Ether*, or *Bromide of Ethyl* (C_4H_5Br) : *Sp. gr. of liquid* 1·4733 at 32°; *of vapour* 3·754; *Boiling pt.* 105°·8.—This compound is usually prepared by adding, by degrees, 12 parts of bromine to 40 parts of alcohol (sp. gr. 0·827) and 1 part of phosphorus, contained in a retort which must be kept cool by immersing it from time to time in cold water; the reaction of bromine and phosphorus upon each other in the presence of the water contained in the alcohol produces hydrobromic ether and phosphethylic acid; and on subjecting the mixture to distillation, hydrobromic ether comes over. It may be purified by agitation with a weak solution of potash, after which it is left to subside; it is then decanted, digested on chloride of calcium, and redistilled.

Bromide of ethyl is a colourless liquid of a peculiar ethereal odour and taste. It boils at 105°·8, though it requires to be heated to 120° before ebullition commences. It remains liquid at —24°. It burns with difficulty, producing a green flame and emitting fumes of hydrobromic acid.

(997) *Hydriodic Ether*, or *Iodide of Ethyl* (C_4H_5I) : *Sp. gr. of liquid* at 32°, 1·9755 ; *of vapour* 5·475; *Boiling pt.* 158°5.—In order to prepare this ether, 100 parts of alcohol are placed in a retort,

small amount of iodine is introduced; phosphorus is added
all quantities at a time until the liquid becomes colourless;
h portion of iodine is then added, and then a fresh quantity
osphorus; this may be continued until about 200 parts of
e and 2 or 3 parts of phosphorus have been added. The
re thus obtained must be cooled by immersing the bulb of
tort after each addition in cold water, otherwise a large pro-
n of the phosphorus will become converted into the red
y, which is not susceptible of being attacked by iodine at low
ratures. After the reaction has terminated the liquid is
ed by the heat of a water-bath, taking care that the iodine
own by its brown colour) is in slight excess. The distillate
d be washed with water, digested on chloride of calcium, and
illed. The reaction which occurs during this operation may
as represented:—

$$\overbrace{{}_4H_6O_2}^{\text{cohol.}}+P_2+5I_2=10\overbrace{C_4H_5I}^{\text{Iodide ethyl.}}+4H_2O_2+2\overbrace{(2HO,C_4H_5O,PO_5)}^{\text{Phosphethylic acid.}}.$$

ann finds it advantageous to place the alcohol and phos-
s in the retort, and to dissolve the iodine in iodide of ethyl;
iquid is allowed to flow gradually into the retort during the
lation, and the operation is thus rendered continuous.

odide of ethyl is a colourless liquid, which, if kept in half-
l bottles, soon undergoes a partial decomposition, and becomes
a from the liberation of iodine. When heated with water to
in a sealed tube, it becomes decomposed into ordinary
and hydriodic acid (Frankland); according to Hofmann, if
l with water and oxide of silver, alcohol and iodide of silver
roduced:—

$$2\,C_4H_5I + Ag_2O_2 + H_2O_2 = 2\,C_4H_6O_2 + 2\,AgI;$$

Wurtz finds that when the anhydrous iodide is heated in a
l tube with oxide of silver, iodide of silver, and ordinary
are formed with facility:—

$$2\,(C_4H_5I) + Ag_2O_2 = (C_4H_5O)_2 + 2\,AgI.$$

If a mixture of equivalent quantities of iodide of methyl and
e of ethyl be treated with oxide of silver, methyl-ethyl ether
duced.

Both the bromide and the iodide of ethyl have been exten-
y employed for the preparation of substitution-compounds
ining ethyl; and it was by decomposing iodide of ethyl in a
d tube by means of zinc, that Frankland succeeded in isolating
hydrocarbon, known as ethyl.

(998) SULPHIDES OF ETHYL.—Alcohol furnishes not less th three remarkable compounds which contain sulphur. One of th $(C_4H_5S)_2$ corresponds in composition to the oxide, or ordinar ether; the second is the *bisulphide of ethyl* $(C_4H_5S_2)_2$—no oxidis representative of this body is known; and the third is *mercapt* (C_4H_5S,HS), a compound which corresponds with alcohol which the oxygen is displaced by sulphur. All these bodies a distinguished by a disgusting alliaceous odour which is extreme powerful and persistent.

Hydrosulphuric Ether, or *Sulphide of Ethyl* $(C_4H_5S)_2$: *Sp. g of liquid* 0·825; *of vapour* 3·1; *Boiling pt.* 163°·4—This compou is easily prepared by decomposing an alcoholic solution of p tosulphide of potassium (469), by transmitting into it the vap of chloride of ethyl, and submitting it to distillation: the distill liquid is to be well washed with water and rectified from chlori of calcium. It is a colourless liquid with an intensely powerf odour of garlic. It forms crystalline compounds with som the metallic chlorides; its compound with corrosive sublim contains $(C_4H_5S,HgCl)$.

Bisulphide of ethyl $[(C_4H_5,S_2)_2$: *Sp. gr. of vapour* 4·27; *Boili pt.* 303°·8] is obtained by distilling 3 parts of sulphethylate potash dissolved in its own weight of water with 2 parts of per sulphide of potassium. The alcoholic solution of this compou gives a yellow precipitate with acetate of lead, and a white wi corrosive sublimate. There appears to be ground for suppos that higher sulphides of ethyl may be obtained.

Mercaptan (C_4H_5S,HS): *Sp. gr. of liquid* 0·835; *of vap* 2·14; *Boiling pt.* 97°.—This compound may be obtained distilling a mixture of equal parts of an aqueous solution sulphethylate of lime, of sp. gr. 1·28, and of a solution potash of the same density, previously saturated by sulphurett hydrogen:—

$$\overbrace{KO,C_4H_5O,S_2O_6}^{\text{Sulphethylate of potash.}}+\overbrace{KS,HS}^{\text{Hydrosulph. potassium.}}=\overbrace{C_4H_5S,HS}^{\text{Mercaptan.}}+2\,\overbrace{KO,S_2O_6}^{\text{Sulph. potash.}}.$$

A better plan, according to Regnault, is to saturate an alcoh solution of potash completely with sulphuretted hydrogen, then to distil it with hydrochloric ether. Mercaptan is a col less, transparent, very mobile liquid, with a most intense repulsive odour of garlic; it is very inflammable, and burns a blue flame. It is sparingly soluble in water, but is diss freely by alcohol and by ether. The solution is neutral to papers, but mercaptan nevertheless presents the characters of a feeble acid. It dissolves sulphur, phosphorus, and iodine with facility. Mercaptan becomes solid at −8°. If a glass rod be moistened with this compound and moved quickly through the air, the cold produced by the evaporation is sufficient to freeze a portion of the remainder. Mercaptan forms with the metals compounds which correspond to the double sulphides of the metals with hydrogen, but they contain ethyl instead of hydrogen, as may be seen by comparing their respective formulæ:—

$$\overbrace{\mathrm{KS,(H)S}}^{\text{Hydrosulphate of potassium.}} \quad ; \quad \overbrace{\mathrm{KS,(C_4H_5)S.}}^{\text{Mercaptide of potassium.}}$$

Mercaptide of potassium is obtained by acting on pure mercaptan with potassium, hydrogen gas being liberated: but it is more particularly on the oxides of the noble metals that the action of mercaptan is remarkable. The name mercaptan (*mercurium captans*) is derived from the energy with which the body unites with oxide of mercury. The mercaptide of mercury (C_4H_5S,HgS) is a white crystalline compound, destitute of odour, and fusible at 185°. It is insoluble in water, but soluble in alcohol: it is easily obtained by digesting oxide of mercury in an alcoholic solution of mercaptan, water being formed, whilst the odour of mercaptan disappears:—

$$2\,(C_4H_5S,HS) + Hg_2O_2 = 2\,(C_4H_5S,HgS) + H_2O_2.$$

The corresponding compound of gold is white and gelatinous; that of platinum is bright yellow, and that of lead (C_4H_5S,PbS) is yellow and crystalline.

(999) Selenium and tellurium each form compounds with ethyl, corresponding to the sulphide of ethyl; they may be obtained by distilling selenide or telluride of potassium with sulphethylate of potash. It is, however, to be remarked that both the selenide and the telluride of ethyl combine with chlorine, bromine, and iodine; and they become oxidized, and form salts with the oxyacids just as though they were metallic bodies. In fact, they present many chemical analogies with the compounds which arsenic, antimony, bismuth, and other metals form with ethyl (1024).

A compound of selenide of ethyl and seleniuretted hydrogen (C_4H_5Se,HSe), corresponding in composition and properties to mercaptan, is formed during the operation of preparing the selenide of ethyl.

(1000) *Cyanide of Ethyl, Hydrocyanic Ether*, or *Propionitrile* ($C_4H_5Cy=C_6H_5N$); *Sp. gr. of liquid* 0·787; *of vapour* 1·928;

Boiling pt. 190°·4.—This compound is obtained in a mann analogous to that directed for the preparation of the foregoi bodies, viz., by the distillation of well-dried sulphethylate potash with two thirds of its weight of cyanide of potassium. A still better method consists in heating a solution of 2 parts iodide of ethyl in 8 of alcohol with 1 part of cyanide of potassium condensing the vapours, and allowing them to fall back into th retort as long as they show any sign of iodine. The product washed with water and rectified by the heat of the water bat It is a colourless, very poisonous liquid, of an alliaceous odo When cyanide of ethyl is treated with a boiling solution of pot the elements of water are assimilated, ammonia is evolved, a propionate of potash is formed :—

$$\overbrace{C_4H_5,C_2N}^{\text{Cyanide of ethyl.}}+KO,HO+H_2O_2=\overbrace{KO,C_6H_5O_3}^{\text{Propionate of potash.}}+H_3N.$$

A similar mode of decomposition is observed to occur with the hydrocyanic ethers when treated with hydrate of pota they all combine with the elements of water and yield one of th acids homologous with formic acid; cyanide of methyl thus yiel acetate of potash :—

$$\overbrace{C_2H_3,C_2N}^{\text{Cyanide of methyl.}}+KO,HO+H_2O_2=\overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}}+H_3N;$$

and cyanide of amyl in like manner furnishes caproate of pota

$$\overbrace{C_{10}H_{11},C_2N}^{\text{Cyanide of amyl.}}+KO,HO+H_2O_2=\overbrace{KO,C_{12}H_{11}O_3}^{\text{Caproate of potash.}}+H_3N.$$

This method of forming the higher terms of the homologous se from those below them is one of considerable interest.

The hydrocyanic ethers (the *nitriles* of some chemists), class, may also be obtained by a process of dehydration, from acids to which they correspond; that is to say, if the ammoni salts of the acids homologous with the formic, be distilled anhydrous phosphoric acid, or be otherwise treated in such a man as to deprive them of 4 equivalents of water, they yield one of hydrocyanic ethers (1165, 1176), thus :—

$$\overbrace{H_4NO,C_2HO_3}^{\text{Formiate of ammonia.}}-2\ H_2O_2=\overbrace{H,C_2N}^{\text{Hydrocyanic acid.}}=(C_2HN,\ \text{Formio-nitri}$$

$$\overbrace{H_4NO,C_4H_3O_3}^{\text{Acetate of ammonia.}}-2\ H_2O_2=\overbrace{C_2H_3,C_2N}^{\text{Cyanide of methyl.}}=(C_4H_3N,\ \text{Acetonitrile)}$$

$$\overbrace{H_4NO,C_6H_5O_3}^{\text{Propionate of ammonia.}}-2\ H_2O_2=\overbrace{C_4H_5,C_2N}^{\text{Cyanide of ethyl.}}=(C_6H_5N,\ \text{Propionitril}$$

and in this manner the hydrocyanic ethers of several series of alcohols have been obtained, although the corresponding alcohols are at present unknown.

The action of potassium upon hydrocyanic ether is remarkable. If the ether be allowed to fall drop by drop upon potassium contained in a flask fitted to a vertical condenser, by means of which any part of the ether which escapes decomposition is allowed to fall back upon the potassium, hydride of ethyl (C_4H_5,H) is formed, whilst cyanide of potassium is produced, and an alkaline base termed *cyanethine* ($C_{18}H_{15}N_3$) remains in the flask (Frankland and Kolbe). This base is polymeric with hydrocyanic ether. It crystallizes from boiling water in pearly scales, and forms salts with the acids. The nitrate ($C_{18}H_{15}N_3,HO,NO_5$) crystallizes in large colourless prisms which are neutral in their reactions.

The hydrocyanic ethers of the other alcohols when treated with potassium appear to furnish compounds homologous with cyanethine.

(*c*) *Ethylic Ethers of the Oxyacids.*

(1001) *Sulphate of Ethyl*, or true *Sulphuric Ether* ($2\,C_4H_5O,S_2O_6$): *Sp. gr. of liquid* 1·120.—This compound was first obtained by Wetherill, by the direct combination of ether with sulphuric anhydride. The vapours of the anhydride are transmitted into a flask containing ether, which is kept cool by ice; the syrupy liquid thus produced is agitated with its own volume of ether, and with four times its bulk of water; when left at rest the sulphate of ethyl rises to the surface; it is purified by agitation with milk of lime, washed, filtered, and dried *in vacuo*. Sulphuric ether is an oily liquid, of burning taste and ethereal odour, resembling that of peppermint. It is scarcely possible to distil it without occasioning its decomposition, as a temperature of 270° or 290° resolves it into alcohol, sulphurous acid, and olefiant gas.

Sweet or *heavy oil of wine* appears to be a mixture of the foregoing compound with some hydrocarbons polymeric with olefiant gas; it is obtained during the later stages of the distillation of ether. If this oil be treated with a solution of potash, it is decomposed; sulphethylate of potash, and a hydrocarbon, termed *etherol* ($C_{32}H_{32}$?) rises to the surface. This hydrocarbon, known also as *light oil of wine*, is polymeric with olefiant gas, and forms a colourless liquid which has a sp. gr. of 0·917; it boils at 536°, and is readily soluble in ether and in absolute alcohol. When exposed to a temperature of $-30°$, it usually deposits semitransparent, friable, colourless prisms of an isomeric hydrocarbon named *etherin*; these fuse at 230°, and boil at 500°; they are lighter than water, in which they are insoluble, but are dissolved freely by alcohol and by ether.

(1002) *Nitric Ether* (C_4H_5O,NO_5): *Sp. gr. of liquid* 1·112, *Boiling pt.* 185°.—Millon obtains this substance by gently heating a mixture of 1 volume of nitric acid, of sp. gr. 1·40 (to which a few grains of nitrate of urea have been added in order to prevent the formation of nitrous acid), and 2 volumes of alcohol, of sp. gr. 0·842; the quantity of the mixture operated on should not exceed a quarter of a pint; under these circumstances the operation proceeds quietly. The first portions of the distillate contain little except alcohol, but as soon as the liquid which distils over becomes turbid on the addition of water, the receiver must be changed, and the nitric ether collected separately: the distillation must be stopped when about three fourths of the liquid have passed over, in order to prevent the ether from becoming mixed with secondary products, which cannot be removed without difficulty. The ether is purified by agitation with a weak solution of alkali, and rectified from chloride of calcium. Nitric ether is a colourless liquid of an agreeable odour, and a taste at first very sweet, but followed by a bitterish after-taste. Its vapour burns with a white luminous flame, and if heated to a little beyond its boiling point, it is decomposed with explosion, on the approach of a light.

Nitrous Ether (C_4H_5O,NO_3): *Sp. gr. of liquid* 0·947; *of vapour* 2·627; *Boiling pt.* 61°.—The *Spiritus Etheris Nitrosi* of the London Pharmacopœia consists of a solution of this ether in alcohol; it has long been used as a therapeutic agent. The safest method of preparing the pure ether consists in introducing into a retort containing copper filings, 1 measure of alcohol (sp. gr. 0·83), to which 1 measure of nitric acid of sp. gr. 1·36 is gradually added. The reaction of nitric acid upon alcohol begins at a very moderate heat, and is apt to become extremely violent, therefore no external heat should be applied during the distillation, after the reaction has once commenced. The vapours which are evolved should be transmitted through a washing bottle containing water, then through a long bent tube filled with chloride of calcium, and finally should be condensed in a flask cooled by ice. Nitrous ether is of a pale yellow colour; it has an agreeable odour of apples. When this ether is kept in contact with water, it speedily becomes decomposed, and an acid is formed which was formerly supposed to be the malic. Debus has, however, shown that the result is a complicated one, nitric, formic, acetic, oxalic, glycolic, and glyoxalic acid ($2\,HO,C_4H_2O_6$) being formed, whilst glyoxal ($C_4H_2O_4$), the aldehyd of glycol, is liberated, together with other aldehyds. (*Phil. Mag.* Nov. 1856.) A solution of the protosulphate of iron becomes blackened when mixed with nitrous ether.

Nitrous ether is decomposed by transmitting its vapour through a red-hot tube, giving rise to a variety of products, among which are hydrocyanate and carbonate of ammonia, derived from the reactions of the nitrogen upon the carbon and hydrogen.

(1003) *Perchloric Ether* (C_4H_5O,ClO_7).—This singular compound cannot be prepared without considerable danger, since it explodes with extraordinary violence when heated to a little beyond 212°; a similar result is produced by friction or by a sudden blow, and sometimes it explodes by merely lifting the vessel which contains it, or even without any assignable cause. In order to obtain it, a few grains of crystallized sulphethylate of baryta are placed in a tube retort with an equal weight of perchlorate of baryta, and are cautiously distilled by the heat of an oil bath, which must not be allowed to exceed 340°. The ether is heavier than water, and has a sweetish pungent taste, somewhat resembling that of cinnamon. Its boiling point is not known with accuracy, but it is above 212°. The explosive character of the compound depends upon the large proportion of oxygen which it contains in union with chlorine, for which the affinity of oxygen is very small, whilst hydrogen has a powerful affinity for both chlorine and oxygen; the oxygen is sufficient to convert the carbon into the form of carbonic oxide, and the hydrogen into water; $C_4H_5O, ClO_7 = 2\,C_2O_2 + 2\,H_2O_2 + HCl$.

(1004) SILICIC ETHERS.—Few of the ethers are more remarkable than those obtained by Ebelmen with silicic acid. In these compounds the polybasic character of the acid is preserved.

Dibasic Silicate of Ethyl ($2\,C_4H_5O,SiO_2)_2$: *Sp. gr. of liquid* 0·933; *of vapour* 7·32.—When absolute alcohol is gradually added to chloride of silicon, a powerful reaction occurs; hydrochloric acid is evolved in abundance, and a colourless liquid is obtained, which when submitted to distillation, at first evolves hydrochloric acid, but the boiling point rises rapidly until it reaches 330°, at which temperature pure dibasic silicate of ethyl distils over. It is a limpid liquid, of a pleasant ethereal odour, and a hot taste resembling that of pepper. It is combustible, and burns with a flame of dazzling whiteness, depositing pulverulent silica The composition of this body is remarkable, 4 volumes of vapour being produced from the compound, $C_{16}H_{20}Si_2O_8$; favouring the hypothesis of the tetratomic character of silicon, with an atomic weight Si=28 (922). This ether is not miscible with water, but is decomposed by it with the separation of gelatinous hydrate of silica. If this decomposition be allowed to take place slowly, by placing an imperfectly closed vessel containing the ether in a moist atmosphere, the silica is gradually deposited in the form of a hard transparent solid, resembling quartz in appearance.

Silicic Ether (C_4H_5O,SiO_2).—A second ether, containing only half the quantity of oxide of ethyl that is present in the foregoing compound, may be procured by acting upon alcohol of sp. gr. 0·838, with chloride of silicon, and distilling; the dibasic silicate is formed at the same time, and the first portions of the distillate consist entirely of this compound; but by degrees the boiling point becomes higher, and when it reaches 660°, the pure monosilicate passes over. The dibasic silicate of ethyl is in fact transformed into the monobasic silicate by the action of the water present in the dilute alcohol; water occasioning the decomposition of the dibasic silicate into the monosilicate, whilst alcohol is set free:—

$$(2\,\overbrace{C_4H_5O,SiO_2)}^{\text{Dibasic silicate of ethyl.}}{}_2+H_2O_2=2\,\overbrace{(C_4H_5O,SiO_2)}^{\text{Monosilicate of ethyl.}}+2\,\overbrace{(C_4H_5O,HO)}^{\text{Alcohol.}}.$$

If more water be added, a viscous compound is obtained, which, according to Ebelmen, contains a third ether, with twice as much silicic acid as the foregoing one.

Tribasic Boracic Ether ($3\,C_4H_5O,BO_3$): *Sp. gr. of liquid* 0·8849; *of vapour* 5·31; *Boiling pt.* 246°.—This ether is obtained by the action of terchloride of boron upon anhydrous alcohol; it is immediately decomposed by water. Boracic acid is readily soluble in anhydrous alcohol with evolution of heat. Ebelmen considers that under these circumstances a second ether is formed, which when pure is solid at ordinary temperatures. It softens at about 100° F., and can be drawn out into long threads. Its composition is not certainly known, but it has been represented as (C_4H_5O, $2\,BO_3$), analogous to ordinary borax.

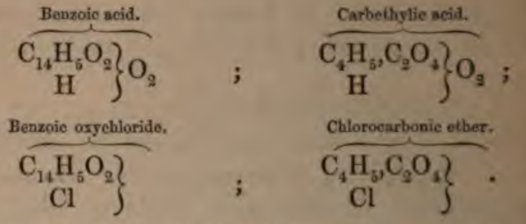
(1005) *Formic Ether* (C_4H_5O,C_2HO_3): *Sp. gr. of liquid* 0·915 at 64°; *of vapour* 2·573; *Boiling pt.* 127°·7.—This ether is readily obtained by distilling 7 parts of dry formiate of soda with 10 of oil of vitriol, and 9 of alcohol of sp. gr. 0·825. Wöhler prepares it from a mixture of 10 parts of starch, with 37 of finely powdered binoxide of manganese, and 15 parts of alcohol, 15 of water, and 30 of oil of vitriol: the whole is distilled by a gentle heat in a capacious retort. The formic acid generated by the oxidation of starch, reacts upon the alcohol at the moment of its forma- n. Formic ether does not mix with the water which accom- ies it; and is purified by washing with water, and rectification on chloride of calcium. Formic ether is also a secondary duct of the reaction of nitric acid upon alcohol. When pure s colourless, and has an agreeable odour and taste, recalling at of peach kernels. If left in contact with water it becomes ily resolved into formic acid and alcohol.

(1006) *Acetic Ether* ($C_4H_5O,C_4H_3O_3$): *Sp. gr. of liquid* 0·89; apour 3·06; *Boiling pt.* 165°.—Acetic acid, if repeatedly dis- lled with alcohol, gives rise to the formation of acetic ether, but e effect is much hastened by the addition of sulphuric acid to e liquid. A mixture of 6 parts of alcohol, 4 of acetic acid, and art of oil of vitriol, yields the ether with facility. When a ume of liquid equal to that of the alcohol employed has come er, the process is stopped; the distillate is washed twice with own bulk of water, and rectified from chloride of calcium. etate of soda or acetate of lead may be substituted for acetic d in the foregoing process, but then a larger quantity of oil of riol is needed. If 6 parts of alcohol be employed, 100 of tate of soda and 15 of oil of vitriol may be used; or 24 parts etate of lead (dried), and 9 of oil of vitriol.

Acetic ether has a burning taste and an agreeable odour, otely resembling that of apples; a small quantity of it appears be contained in several varieties of wine. Water dissolves ut one-seventh of its bulk of it. Acetic ether is a good solvent the essential oils, for the resins, and for pyroxylin. A mixture this ether with an alcoholic solution of hydrate of potash, is ediately decomposed into acetate of potash and alcohol. etic ether dissolves chloride of calcium readily, and forms with crystallizable compound, which yields the ether unchanged on application of heat.

(1007) *Butyric Ether* ($C_4H_5O,C_8H_7O_3$ *Sp. gr. of liquid* 0·9041; pour 4·04; *Boiling pt.* 238°·8) is remarkable for the facility which it may be formed. If a mixture of 2 parts of alcohol 2 of butyric acid be agitated with 1 part of oil of vitriol, ch may even be diluted with an equal bulk of water, the liquid, nding, separates into two layers, the upper of which is butyric er. This ether is nearly insoluble in water, and when diluted h alcohol has the odour of pine apple, constituting, indeed, t is sold as *pine-apple oil*. In order to purify the ether, it be agitated with water, and rectified after standing upon ide of calcium.

Chlorocarbonic Ether (C_4H_5O,C_2ClO_3): *Sp. gr. of liquid* 1·13 *of vapour* 3·823 ; *Boiling pt.* 201°.—This compound is obtained absorbing phosgene gas (327) by absolute alcohol, and rectify the product from powdered litharge and chloride of calcium. is a colourless, very limpid liquid, which emits a suffocating od and irritates the eyes powerfully. Its vapour burns with a gre flame. It is not soluble in cold water, but is decomposed boiling water. Gerhardt represents this compound as an ox chloride, which bears the same relation to carbethylic a that benzoic oxychloride (chloride of benzoyl) does to benz acid :—



$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}O_2}^{\text{Benzoic acid.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5,C_2O_4\\H\end{matrix}\right\}O_2}^{\text{Carbethylic acid.}} \; ;$$

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right\}}^{\text{Benzoic oxychloride.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_4H_5,C_2O_4\\Cl\end{matrix}\right\}}^{\text{Chlorocarbonic ether.}} \; .$$

(1011) *Cyanic Ether* (C_4H_5O,C_2NO) : *Sp. gr. of liquid* 0·89 *of vapour* 2·475 ; *Boiling pt.* 140°.—This ether may be prepar by distilling cyanate of potash with the sulphethylate of that ba It is an extremely pungent volatile liquid of high refracti power. Cyanic ether when decomposed by hydrate of pota undergoes a remarkable transformation, in consequence of whi it is converted into a new base, ethylia, $C_4H_7N, = \left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}$ which corresponds to ammonia in which one atom of hydrogen been displaced by ethyl (C_4H_5), the organic radicle of eth (Wurtz, *Ann. de Chimie*, III. xxx. 447.)

$$\overbrace{C_4H_5O,C_2NO}^{\text{Cyanic ether.}} + \overbrace{2\,(KO,HO)}^{\text{Hydrate of potash.}} = \overbrace{2\,KO,C_2O_4}^{\text{Carbonate of potash.}} + \overbrace{C_4H_5,H_2N}^{\text{Ethylia.}}.$$

A similar decomposition ensues when the cyanic ethers of t other alcohols are treated with hydrate of potash, a series alkalies homologous with ethylia being formed. Thus, start with hydrated cyanic acid, which contains hydrogen instead of of the radicles of the ethers :—

$$\overbrace{HO,C_2NO}^{\text{Cyanic acid.}} + 2\,(KO,HO) = 2\,KO,C_2O_4 + \overbrace{H,H_2N}^{\text{Ammonia.}}$$

$$\overbrace{C_2H_3O,C_2NO}^{\text{Methyl-cyanic ether.}} + 2\,(KO,HO) = 2\,KO,C_2O_4 + \overbrace{C_2H_3,H_2N}^{\text{Methylia.}}$$

ent; alcohol, and a substance soluble in alcohol but insoluble water, crystallizing in beautiful pearly tables, is formed: this was originally termed *oxamethane*, but it is now admitted to *mic ether*, or the ether of amidated oxalic acid ($HO,H_2NC_4O_5$; :—

$$\overbrace{2C_4H_5O,C_4O_6}^{\text{Oxalic ether.}} + H_3N = \overbrace{C_4H_5O,H_2NC_4O_5}^{\text{Oxamic ether.}} + \overbrace{C_4H_5O,HO}^{\text{Alcohol.}}.$$

If equal parts of oxalethylate of potash and sulphomethylate of ash be thoroughly dried, then mixed and submitted to distil- ion, a curious double ether (*methyl-ethyloxalic ether*, ($C_2H_3O,$ H_5O,C_4O_6) is obtained. It forms a yellowish oil, heavier than er, of sp. gr. 1·127, boiling at about 330°, and emitting a vapour p. gr. 4·67.

(1010) *Carbonic Ether* ($2C_4H_5O,C_2O_4$): *Sp. gr.* 0·975; *of vapour* 9; *Boiling pt.* 257°.—This ether cannot be obtained by the nary mode of preparing these compounds. It may be formed eating carbonate of silver with iodide of ethyl in a closed e; but it is generally procured by heating sodium or potassium oxalic ether, in which case carbonic oxide is disengaged ndantly, whilst carbonic ether distils over, and oxalate of the li remains in the retort. This reaction does not admit of a ple expression by an equation. Carbonic ether is a very mobile id, of a sweet aromatic odour; it is not very inflammable; but readily decomposed by an alcoholic solution of potash. When ted in a sealed tube with an alcoholic solution of ammonia, hol and carbamic ether (urethane) are formed; and if the perature be raised to about 356°, the excess of ammonia slowly verts the carbonic ether into alcohol and urea, or carbamide tanson); both decompositions being analogous to those oxalic ether undergoes with greater facility by the same gents:—

$$\overbrace{2C_4H_5O,C_2O_4}^{\text{Carbonic ether.}} + H_3N = \overbrace{C_4H_5O,H_2NC_2O_3}^{\text{Carbamic ether.}} + \overbrace{C_4H_5O,HO}^{\text{Alcohol.}}$$

$$\overbrace{H_5O,H_2NC_2O_3}^{\text{Carbamic ether.}} + H_3N = \overbrace{H_4N_2C_2O_2}^{\text{Carbamide (Urea).}} + \overbrace{C_4H_5O,HO}^{\text{Alcohol.}}$$

rethane, or *carbamic ether* ($C_4H_5O,H_2NC_2O_3$): *Boiling pt.* 356°; *of vapour* 3·14.—This is a substance which resembles ceti in appearance; it evinces a remarkable disposition to e, and forms large transparent leaflets, which are fusible 212°, and very soluble in alcohol and ether. If distilled st state, it gives off large quantities of ammonia.

(1012) *Cyanuric Ether* ($3\,C_4H_5O,C_6N_3O_3$): *Sp. gr. of* 7·4.—This compound is obtained by distilling a mixture of ethylate and cyanurate of potash, by the heat of an oil-bath. is polymeric with cyanic ether: but it is solid at ordinary peratures, and may be obtained from its solution in ether brilliant crystals, which melt at 205°, forming a liquid than water, which boils at 487°, and may be distilled unalte When treated with hydrate of potash, it yields ethylia as ultimate result. The cyanuric ethers of the other alcohols the corresponding alkalies when similarly treated, the final ducts being identical with those which are furnished when cyanic ethers of the same series are similarly decomposed:—

$$3\,\overbrace{C_4H_5O,C_6N_3O_3}^{\text{Cyanuric ether.}}+6\,(KO,HO)=3\,(2\,KO,C_2O_4)+3\,\overbrace{(C_4H_5,H}^{\text{Ethylia.}}$$

Allophanic Ether ($C_4H_5O,C_4H_3N_2O_5$).—This compound long mistaken for cyanuric ether. It is obtained by transmitt the vapours of hydrated cyanic acid into alcohol. It is a crystalline, colourless, tasteless, inodorous body which is insol in cold water, but is soluble in boiling water, in ether, and boiling alcohol. It is soluble in cold baryta water, which conv it into alcohol, and a new salt, allophanate of baryta ($C_4H_3N_2O_5$). Allophanic acid is not known except in combinat

(*d*) *Ethers not derived from Ethylic Alcohol.*

(1013) METHYLIC ETHER, or *Oxide of Methyl* ($(C_2H_3O)_2$ *gr. of vapour* 1·617.—By distilling 1 part of pyroxylic spirit 4 parts of oil of vitriol, a colourless gas, homologous with eth ether, is disengaged. It is accompanied by carbonic and sul rous acids, which may be removed by allowing the gaseous mix to stand for twenty-four hours in contact with slaked lime. seous methylic ether has a peculiar oppressive ethereal odour; freely soluble in water, which dissolves about 37 times its bul the gas, and acquires its odour and pungent ethereal taste. still more soluble in alcohol. This gas is very inflammable, burns with a pale flame; it is liquefiable at a temperature of – and boils at –6° (Berthelot). This substance, it should be obse is metameric with alcohol, with which it corresponds, both molecular number and in the density of its vapour. Comp of methyl may be obtained with chlorine, bromine, iodin sulphur, forming chloride, bromide, iodide, and sulphide of me all these bodies are inflammable: the chloride is gase inary temperatures; the bromide and the iodide are volatile ids of considerable density. All these compounds are preed like the corresponding compounds of ethyl. Combinas of oxide of methyl with the oxyacids also exist, forming class of compounds parallel with the ethylic oxyacid ethers: s we have sulphate, nitrate, oxalate, acetate of methyl, and &c.

(1014) *Methyl-Sulphuric Ether*, or *Sulphate of Methyl* ($2\,C_2H_3O$, O_3; *Boiling pl.* 370°) is procured by transmitting dry methylic her over sulphuric anhydride, or by distilling 1 part of pyroxylic rit with 8 or 10 parts of oil of vitriol; in the latter process the her passes over as a tasteless oily liquid, and collects in the eiver. It must be washed with cold water, digested on quickme to free it from sulphurous acid and water, and then rectified. is thus obtained as a colourless liquid which gives off a vapour taining 2 atoms of oxide of methyl and 1 of sulphuric acid O_3) in 4 volumes. It is slowly decomposed by water in the ld, but is quickly resolved by it at the boiling point into wood rit and sulphomethylic acid.

Methyl-Acetic Ether, or *Acetate of Methyl* ($C_2H_3O,C_4H_3O_3$, *iling pl.* 133°) is formed abundantly during the destructive llation of wood, and enters largely into the composition of de wood spirit. It is a colourless liquid, of an agreeable real odour, and is freely soluble in water. The hydrated alies decompose it into acetic acid and wood spirit. It may be ained by distilling 2 parts of wood spirit with 1 part of contrated acetic acid, and one of oil of vitriol; the crude product rectified from chloride of calcium, which retains the unchanged od spirit.

Methyl-Oxalic Ether, or *Oxalate of Methyl* ($2\,C_2H_3O,C_2O_6$): *ling pl.* 322°; *Sp. gr. of liquid at* 122°, 1·1566.—This compound olid at ordinary temperatures, and may be sublimed without mity. It may be obtained by mixing 1 part of crude wood rit with one of oil of vitriol, and distilling the mixture with 2 ts of binoxalate of potash. The materials should be allowed to ain in contact for 24 hours before the distillation is proceeded h. A volatile liquid first passes over, followed by crystals of the er. When these crystals begin to appear in the neck of the ort, the receiver must be changed, and the distillation carried on long as the crystals continue to be formed. These crystals must purified by strong pressure between folds of blotting-paper, and afterwards be maintained for some time in a melted state by ntle heat, in order to drive off adhering volatile matters.

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Methyl-Oxalic Ether, or *Oxalate of Methyl* ($2\,C_2H_3O, C_2O_6$): *Boiling pt.* 322°; *Sp. gr. of liquid at* 122°, 1·1566.—This compound is solid at ordinary temperatures, and may be sublimed without difficulty. It may be obtained by mixing 1 part of crude wood spirit with one of oil of vitriol, and distilling the mixture with 2 parts of binoxalate of potash. The materials should be allowed to remain in contact for 24 hours before the distillation is proceeded with. A volatile liquid first passes over, followed by crystals of the ether. When these crystals begin to appear in the neck of the retort, the receiver must be changed, and the distillation carried on as long as the crystals continue to be formed. These crystals must be purified by strong pressure between folds of blotting-paper, and must afterwards be maintained for some time in a melted state by a gentle heat, in order to drive off adhering volatile matters.

A compound of oxide of methyl with one of the org has been discovered ready formed in the vegetable kingd stituting, in combination with salicylic acid, *salicylate* (C_2H_3O, $C_{14}H_5O_5$), the essential oil procured from the *Bet* a species of birch, and from the *winter green* (*Gaultheria bens*): a compound exactly resembling the natural oil is by distilling a mixture of wood spirit with salicylic and acids. This compound possesses the power of uniting w like an acid (1268).

(1015) The following table shows the composition of the physical properties of the more important methy The densities to which an asterisk is affixed were taken a

Methyl = C_2H_3.	Formulæ.	Boiling point, °F.	Specifi
			Liquid.
Oxide of methyl . .	$(C_2H_3O)_2$	—6	
Sulphide " . .	$(C_2H_3S)_2$	105·8	0·845
Bisulphide " . .	$(C_2H_3S_2)_2$	about 240	1·048
Chloride " . .	C_2H_3,Cl	—7·6	
Bromide " . .	C_2H_3,Br	55·5	1·644*
Iodide " . .	C_2H_3,I	111·4	2·1992*
Cyanide " . .	C_2H_3,C_2N	170·6	
Sulphate " . .	$2\,C_2H_3O,S_2O_6$	370	1·324
Nitrate " . .	C_2H_3O,NO_5	151	1·182
Borate " . .	$3\,C_2H_3O,BO_3$	161·6	0·955
Formiate " . .	$C_2H_3O,C_2\,H\,O_3$	92·1	0·9984*
Acetate " . .	$C_2H_3O,C_4\,H_3O_3$	133·3	0·9562*
Butyrate " . .	$C_2H_3O,C_8\,H_7O_3$	204·6	0·9209*
Valerate " . .	$C_2H_3O,C_{10}H_9O_3$	241·1	0·9015*
Cyanate " . .	$C_2H_3O,C_2\,N\,\,O$	about 104	
Cyanurate " . .	$3\,C_2H_3O,C_6\,N_3O_3$	525	
Benzoate " . .	$C_2H_3O,C_{14}H_5O_3$	389·3	
Oxalate " . .	$2\,C_2H_3O,C_4\,\,\,O_6$	321·8	1·1566
Salicylate " . .	$C_2H_3O,C_{14}H_5O_5$	431·6	1·18

(1016) *Tritylic, Tetrylic, Amylic, and Octylic Et* *Tritylic Ether* was obtained by Chancel, but it is littl and its derivatives have not yet been investigated.

2. *Tetrylic* (butylic) *Ether* was first described by Kol of the products of the voltaic decomposition of valerate o Since that time, Wurtz has published a memoir on t of the tetrylic series, to which the reader is referred for tion of their properties (*Ann. de Chimie*, III. xlii. 129).

3. *Amylic Ether* $(C_{10}H_{11}O)_2$, *Boiling pt.* 349°, is obtain small quantity by the distillation of fousel oil with sulph since by this method the greater part of the alcohol is *into* hydrocarbons polymeric with olefiant gas. Balard w

he also procured it by decomposing chloride of amyl ($C_{10}H_{11}Cl$) by means of a concentrated solution of potash: the mixture is to be sealed up in a tube and heated for some time to 212°. The liquid which floats upon the surface has a fragrant odour, and boils at about 233°. It is, however, doubtful, according to Williamson, whether this be not amylethylic ether. No analysis of it has been made. It is probable that some of the compound ethers of the amylic series are the bodies to which the odour and flavour of certain fruits belong (991), but they present no special points of interest, and therefore need no detailed description. They may be procured by methods analogous to those which were described when treating of the different ethylic ethers. The amylic series was carefully investigated by Cahours (*Ann. de Chimie*, II. lxx. and lxxv).

The following table contains the principal ethers of the tetrylic and amylic groups:—

	Tetrylic (Butylic) Series.				Amylic Series.			
	Formulæ.	Boiling point, ° F.	Sp. gr.		Formulæ.	Boiling point, ° F.	Sp. gr.	
			Liquid.	Vapour.			Liquid.	Vapour.
Oxide					$(C_{10}H_{11}O)_2$	348·8		
Sulphide					$(C_{10}H_{11}S)_2$	420·8		6·3
Bisulphide					$(C_{10}H_{11}S_2)_2$	480 ?	0·918	
Chloride	C_8H_9Cl	160			$C_{10}H_{11},Cl$	215		3·77
Bromide	C_8H_9Br	192	1·274	4·72	$C_{10}H_{11},Br$			
Iodide	C_8H_9I	249·8	1·604	6·217	$C_{10}H_{11},I$	294·8	1·511	6·675
Cyanide	C_8H_9,Cy	257	0·810	2·892	$C_{10}H_{11},C_2N$	294·8	0·806	3·335
Nitrate	C_8H_9O,NO_5	266			$C_{10}H_{11}O,NO_5$	298·4	0·994	
Formiate					$C_{10}H_{11}O,C_2\ HO_3$	237	0·884	
Acetate	$C_8H_9O,C_4H_3O_3$	237	0·884	4·073	$C_{10}H_{11}O,C_4\ H_3O_3$	279	0·869	4·458
Valerate					$C_{10}H_{11}O,C_{10}H_9O_3$	368	0·864	6·17
Carbonate					$2\,C_{10}H_{11}O,C_2\quad O_4$	435	0·914	
Oxalate					$2\,C_{10}H_{11}O,C_4\quad O_6$	503		8·4

4. Bouis has examined (*Ann. de Chimie*, III. xliv. 128) several of the ethers of the *octylic* (caprylic) series: many of them possess a very agreeable and fragrant odour, which may possibly lead to their employment as perfumes; but they do not present sufficient importance to require further notice in this work. These ethers may generally be obtained by methods analogous to those directed to be used for the preparation of the corresponding methylic and ethylic ethers.

§ IV. ACTION OF CHLORINE ON THE ETHERS AND ALCOHOLS.

(1017) Chlorine exerts a powerful action upon the alcohols, and upon all their derivatives which contain hydrogen, forming by substitution numerous compounds, in which a certain number of atoms of hydrogen are displaced by a corresponding number of atoms of chlorine. Similar effects are produced by bromine and by iodine, though the action of these elements is less energetic. Solar light greatly increases the facility with which the reaction is effected. The general laws by which these substitutions are regulated will be best understood by the description of a few of the most important compounds thus formed.

(*a*) *Chlorinated Derivatives from Wine Alcohol.*

(1018) *Dichlorinated Ether* $(C_4H_3Cl_2,O)_2$; *Sp. gr.* 1·5008.—When dry chlorine is passed into anhydrous ether, abundance of hydrochloric acid is formed; 2 of the 5 atoms of hydrogen in each half of the molecule of ether are displaced, and in their stead 2 atoms of chlorine enter into the compound. 8 atoms of chlorine, and 1 molecule of ether, thus produce 4 atoms of hydrochloric acid, and 1 molecule of this new body :—

$$\overbrace{\left(C_4\overset{H_3}{\underset{H_2}{}}O\right)_2}^{\text{Ether.}} + 4\,Cl_2 = 4\,HCl + \overbrace{\left(C_4\overset{H_3}{\underset{Cl_2}{}}O\right)_2}^{\text{Dichlorinated ether.}}.$$

It forms a heavy, colourless, oily liquid, neutral to litmus paper, with an odour and taste resembling that of fennel; at 284° it undergoes decomposition before it begins to boil, and by contact with water it is gradually converted into acetic and hydrochloric acids. It was regarded by Liebig as a compound of the same order as acetic acid, and he termed it *oxychloride of acetyl*, $(C_4H_3,Cl_2O)_2$; 6 atoms of water would produce, with 1 molecule of this substance, 2 atoms of monohydrated acetic acid and 4 of hydrochloric acid; $\left(C_4\overset{H_3}{\underset{Cl_2}{}}O\right)_2 + 3H_2O_2 = 2(HO,C_4H_3O_3) + 4\,HCl$. An alcoholic solution of potash immediately produces a similar decomposition, chloride of potassium and acetate of potash being formed.

Perchlorinated Ether $(C_4Cl_5O)_2$: *Sp. gr. of solid* 1·9; *Fusing pt.* 156°.—If ether, saturated with chlorine, be exposed in a vessel with excess of the gas, to the direct rays of the sun, a crystalline body is formed, which is soluble in hot alcohol, and crystallizes on cooling in octohedra with a square base. This substance represents ether, in which the whole of the hydrogen has been displaced by chlorine. Under certain circumstances the perchlorinated ether, at the moment of its formation, is resolved into sesquichloride of carbon, and into a body corresponding to aldehyd, but in which all the hydrogen has been displaced by chlorine: and a similar transformation occurs when the vapour of the chlorinated ether is exposed to a temperature of about 592°:—

$$\overbrace{(C_4Cl_5O)_2}^{\text{Perchlorin. ether.}} = \overbrace{C_4Cl_6}^{\text{Sesquichlor. Carb.}} + \overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}}.$$

An alcoholic solution of potash decomposes perchlorinated ether, but the reaction is complicated, owing to the presence of compounds derived from the alcohol employed.

(1019) The action of chlorine upon chloride of ethyl is more regular; with suitable care it is possible to obtain compounds in which each equivalent of hydrogen is successively removed, and its place supplied by chlorine, as shown in the table given at page 64.

(1020) *Action of Chlorine upon Compound Ethers.*—The foregoing examples are true cases of substitution; but in some rare instances the chlorine unites directly with the compound, producing a new chlorinated body, without separation of hydrogen or formation of hydrochloric acid; a case of this kind is presented in pyromucic ether ($C_4H_5O,C_{10}H_3O_5$), each molecule of which absorbs 4 atoms, or rather more than its own weight of chlorine, and from a crystalline solid becomes converted into a colourless syrupy liquid, $C_4H_5O,C_{10}H_3Cl_4O_5$. A more familiar example is offered in the direct union of chlorine and olefiant gas; these two gases, when mingled in equal measures, combine to form the oily liquid discovered by the Dutch chemists, and which, by the continued action of chlorine, yields a series of compounds (400), the last member of which is Faraday's sesquichloride of carbon.

The following table exhibits in one view the effect of chlorine in its successive stages upon ether, and some of its derivatives and compounds:—

Chlorinated Ethylic Ethers.

	Normal Ethers.	Dichlorinated.	Perchlorinated.	Various stages.
Alcohol	C_4H_5O,HO			$C_4HCl_5O_2$
Ether	$(C_4H_5O)_2$	$(C_4H_3Cl_2O)_2$	$(C_4Cl_5O)_2$	
Carbonic ether .	$2\,C_4H_5O,C_2O_4$	$2\,C_4H_3Cl_2O,C_2O_4$	$2\,C_4Cl_5O,C_2O_4$	
Oxalic ether . .	$2C_4H_5O,C_4O_6$		$2\,C_4Cl_5O,C_4O_6$	
Formic ether .	$C_4H_5O,C_2H\ O_3$	$C_4H_3Cl_2O,C_2HO_3$	C_4Cl_5O,C_2ClO_3	
Acetic ether .	$C_4H_5O,C_4H_3O_3$	$C_4H_3Cl_2O,C_4H_3O_3$	$C_4Cl_5O,C_4Cl_3O_3$	
Trichloracetic do.	$C_4H_5O,C_4Cl_3O_3$		$C_4Cl_5O,C_4Cl_3O_3$	$C_4HCl_4O,C_4Cl_3O_3$
Benzoic do. . .	$C_4H_5O,C_{14}H_5O_3$			$C_4H_3Cl_2,C_{14}H_5O_3$
Pyromucic do .	$C_4H_5O,C_{10}H_3O_5$			$C_4H_5O,C_{10}H_3Cl_4O_5$

Experiment shows that, whether ether be free or in combination, the first 2 atoms of hydrogen are more readily removed from the atom of ethyl than the others, as indeed might be expected from the facility with which alcohol loses 2 atoms of hydrogen by oxidation, in the manufacture of acetic acid. All the compounds indicated in the third column of the table are represented as containing $C_4H_3Cl_2O$; and when any one of these is submitted to the action of an alcoholic solution of hydrate of potash, it is decomposed; and acetate of potash, along with chloride of potassium, is found among the products. This circumstance can only be explained by supposing that, whenever the compound ethers of an organic acid into the composition of which hydrogen enters are submitted to the action of chlorine, the hydrogen is in the first instance displaced from the ether; and subsequently, by prolonged continuance of the action, the displacement extends to the hydrogen contained in the acid of the compound. The mode in which the new bodies undergo decomposition, in many instances affords proof that the displacement is effected in this order. When, for example, chlorinated formic ether is decomposed by an alcoholic solution of potash, chloride of potassium, and acetate and formiate of the base, are the result:—

$$4\,(KO,HO)+\overbrace{C_4H_3Cl_2O,C_2HO_3}^{\text{Dichloroformic ether.}}=\overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}}+2\,KCl+\overbrace{KO,C_2HO_3}^{\text{Formiate of potash.}}+2H_2O_2.$$

Now the compound $C_4H_3Cl_2O$, when decomposed by potash, yields acetate of potash and chloride of potassium (1018), so that the formiate is evidently derived from undecomposed formic acid.

When chlorine is made to act upon the ethers under the conjoined influence of the sun's rays and of a high temperature, the whole of the hydrogen, both of the ether and of the acid combined with it, is displaced. These perchlorinated compound ethers, such as the perchloracetic ether ($C_4Cl_5O,C_4Cl_3O_3$) and perchloroformic ether (C_4Cl_5O,C_2ClO_3), are very unstable. They are readily decomposed by elevation of temperature, and by alcohol, as well as by solutions of ammonia, and of the fixed alkalies. When the perchlorinated ethylic ethers are subjected to a high temperature, the products obtained vary with the nature of the acid combined with the ether; but amongst these products, perchloraldehyd ($C_4Cl_4O_2$) is always present. This compound is doubtless derived from the compound $(C_4Cl_5O)_2$ which all those bodies contain, and which, at an elevated temperature (1018), yields sesquichloride of carbon C_4Cl_6 and perchloraldehyd ($C_4Cl_4O_2$). When the decomposition is effected by alcohol, or by an alcoholic solution of potash, amongst other bodies trichloracetic acid ($HO,C_4Cl_3O_3$), or the products of its decomposition, is always found. This substance is the result of the action of water upon perchloraldehyd, hydrochloric acid being liberated, as is shown thus:—

$$\overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}}+H_2O_2=\overbrace{HO,C_4Cl_3O_3}^{\text{Trichloracetic acid.}}+HCl\,;$$

n ammonia is made to act upon one of these perchlorinated richloracetamide, which is always one of the products, is by the following reaction upon perchloraldehyd :—

$$\overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}}+2\,\overbrace{H_3N}^{\text{Ammonia.}}=\overbrace{C_4Cl_3H_2NO_2}^{\text{Trichloracetamide.}}+H_4NCl.$$

ours finds that the chloromethylic ethers are subject to general modes of decomposition, though of course the products differ from those yielded by the ethylic series.

requently happens, however, that the compound produced action of chlorine does not correspond in composition to ly which furnishes it; for in these cases the number of of hydrogen which are removed is greater than the number s of chlorine which enter into the compound. An example kind occurs when dry chlorine is transmitted through ous alcohol, when the substance described by Liebig under ne of chloral is formed.

hen the compound ethers are treated with a chlorinating and ing body like terchloride of phosphorus, the results are t; a portion of the oxygen, both of the acid and of the eing removed, whilst a corresponding number of atoms of e supplies its place, and the compound becomes split into w bodies. Thus Béchamp found acetic ether to yield e of ethyl and acetic oxychloride, whilst phosphorous acid med :—

$$\overbrace{(C_4H_5O,C_4H_3O_3)}^{\text{Acetic ether.}}+2\,PCl_3=3\,\overbrace{(C_4H_5Cl)}^{\text{Chloride ethyl.}}+3\,\overbrace{(C_4H_3O_2Cl)}^{\text{Oxychlor. acetyl.}}+2\,PO_3.$$

21) CHLORAL, or *Trichloraldehyd* ($C_4Cl_3HO_2$) : *Sp. gr. of* 1·502; *of vapour* 5·13; *Boiling pt.* 201°.—When pure ous alcohol is submitted to the action of well-dried chlo- is decomposed; but 8 atoms of chlorine are required for composition of a single atom of alcohol; a copious dis- ment of hydrochloric acid occurs, and chloral is formed. dy, however, does not correspond in composition to , but to aldehyd; 2 atoms of hydrogen having been re- without any corresponding substitution of chlorine, whilst er 3 atoms of hydrogen have been displaced by chlorine in al manner. These relations will be at once perceived by ing the formulæ;

Alcohol . . . . . . $C_4H_6O_2$ or C_4H_5O,HO
Aldehyd . . . . . . $C_4H_4O_2$ or C_4H_3O,HO
Chloral . . . . . . $C_4Cl_3HO_2$, or C_4Cl_3O,HO ;

and the reaction is represented by the equation :—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}}+4\ Cl_2 = \overbrace{C_4Cl_3HO_2}^{\text{Chloral.}}+5\ HCl.$$

If chlorine be passed into dilute instead of into anhydrous alcohol, no chloral is formed, but instead of it aldehyd, acetic acid, and hydrochloric acid are produced. In this case aldehyd appears to be the compound formed, and by a secondary reaction of aldehyd upon water at the moment of its formation, it appropriates 2 equivalents of oxygen from the water, whilst the chlorine removes the corresponding quantity of hydrogen :—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}}+\ Cl_2 = \overbrace{C_4H_4O_2}^{\text{Aldehyd.}}+2\ HCl;\ \text{and}$$

$$\overbrace{C_4H_4O_2}^{\text{Aldehyd.}}+H_2O_2+Cl_2 = \overbrace{C_4H_4O_4}^{\text{Acetic acid.}}+2\ HCl.$$

In order to obtain chloral in a state of purity, the alcohol is subjected for many hours to a current of chlorine, which is transmitted so long as it is absorbed. It is necessary at first to keep the alcohol cool, but afterwards the temperature must be gradually raised until the liquid boils. The crude product is mixed with three times its bulk of oil of vitriol, and distilled at a gentle heat. This operation must be repeated, and the product finally distilled over quicklime. Stædeler finds that chloral may also be formed by distilling a mixture of one part of starch (or sugar) with 7 parts of hydrochloric acid and 3 of peroxide of manganese; formic and carbonic acids, and other bodies, accompany it.

Chloral is in many respects a remarkable body. It is a colourless, oily-looking fluid, of a peculiar penetrating odour, which produces a flow of tears; when dropped upon paper it leaves a transient greasy stain. It is soluble in water, alcohol, and ether. If mixed with a small quantity of water, much heat is extricated, and a crystalline hydrate is formed. One of its most singular properties is the change which it undergoes spontaneously when kept; in a few days it becomes converted into a tough white porcellanous-looking mass, isomeric with the liquid form, into which, by distillation, it can be again converted. This white substance is insoluble in alcohol, in ether, and in water; but by contact with water it is gradually converted into the crystallized e of chloral. The facility of thus effecting its transforma- to isomeric modifications indicates a certain resemblance to d in the instability of its molecular arrangement.

alcoholic solution of potash converts chloral immediately rmiate of potash and chloroform :—

$$\overbrace{C_4Cl_3HO_2}^{\text{Chloral.}} + KO,HO = \overbrace{KO,C_2HO_3}^{\text{Formiate of potash.}} + \overbrace{C_2HCl_3}^{\text{Chloroform.}}.$$

ct cannot, however, be supposed to indicate much respect- e grouping of the component elements of chloral, the le equilibrium of which is evidenced by the facility with which spontaneously passes from the liquid to the solid condi- There is no doubt that the arrangement is very different in two forms, and if thus, whilst unsolicited by any extraneous al forces, its molecular arrangement is so readily altered, it ous that the results of its decomposition under the influence erful chemical agents will throw but little light upon the le grouping of its constituent elements.

22) *Perchloraldehyd* ($C_4Cl_4O_2$) *: Sp. gr. of liquid* 1·603 ; *of* 6·32 ; *Boiling pt.* 244°.—This body is obtained by trans- the vapour of perchlorinated ether $(C_4Cl_5O)_2$ through tubes (1018), a mixture of sesquichloride of carbon and raldehyd being the result. The two compounds may be ted by distillation, since the chloride of carbon is the less of the two. Perchloraldehyd is also always one of the pro- of the decomposition of the compound chlorinated ethylic by heat (1020), of which the following may be taken as les :—

$$\overbrace{C_4Cl_5O,C_2ClO_3}^{\text{Perchloroformic ether.}} = \overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}} + \overbrace{C_2O_2Cl_2}^{\text{Phosgene.}}.$$

$$\overbrace{C_4Cl_5O,C_4Cl_3O_3}^{\text{Perchloracetic ether.}} = 2\ \overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}}.$$

$$\overbrace{2\ C_4Cl_5O,C_4O_6}^{\text{Perchloroxalic ether.}} = 2\ \overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}} + \overbrace{C_2O_2Cl_2}^{\text{Phosgene.}} + \overbrace{C_2O_2}^{\text{Carb. oxide.}}.$$

transparent, fuming, volatile liquid, which emits a suffo- odour, and turns the skin white if allowed to fall upon it. decomposes it gradually into hydrochloric and trichloracetic —

$$\overbrace{C_4Cl_4O_2}^{\text{Perchloraldehyd.}} + H_2O_2 = \overbrace{HO,C_4Cl_3O_3}^{\text{Trichloracetic acid.}} + HCl.$$

omine resembles chlorine in *its action* upon alcohol, form-

ing *bromal* ($C_4Br_3HO_2$), which is a colourless oil of sp. gr.
boiling above 212°.

(*b*) *Chlorinated Derivatives from other Alcohols and their E*

It will be unnecessary to enter into any detailed descri
of the innumerable compounds which may be formed fro
simple and compound ethers of the other alcohols, by the s
tution of chlorine, bromine, and iodine for hydrogen; for, wi
exception, which occurs in the case of chloroform, they p
but little to arrest the attention of the chemist. They have
minutely studied by Malaguti, Cahours, and Cloez, to
various papers in the *Annales de Chimie*, the reader is refer
further information on the subject.

(1023) Chloroform (C_2HCl_3): *Sp. gr. of liquid* 1·4
vapour 4·2; *Boiling pt.* 142°.—This interesting compound
duced by a variety of reactions: 1. when chlorine is made
upon chloride of methyl, the following change occurs:—

$$\overbrace{C_2H_3Cl}^{\text{Chlor. methyl.}} + 2\,Cl_2 = \overbrace{C_2HCl_3}^{\text{Chloroform.}} + 2\,HCl.$$

2. Another remarkable mode of its formation has been poin
by Dumas, who finds that an oily liquid consisting of chlo
and bichloride of carbon, is slowly produced by mixing to
in diffused daylight 4 measures of chlorine with 1 mea
marsh gas, which latter must be diluted with an equal b
carbonic acid in order to prevent the danger of spontane
plosion. The chloroform and the bichloride vary in propor
different experiments, but the mode of their formation m
illustrated by the subjoined equation:—

$$2\,C_2H_4 + 7\,Cl_2 = C_2HCl_3 + C_2Cl_4 + 7\,HCl.$$

3. Chloroform is also produced during the decomposition
trichloracetates by the hydrated alkalies:—

$$\overbrace{KO,C_4Cl_3O_3}^{\text{Trichloracet. potash.}} + KO,HO = 2\,\overbrace{KO,C_2O_4}^{\text{Carb. potash.}} + \overbrace{C_2HCl_3}^{\text{Chloroform.}}.$$

4. Also by the action of the hydrated alkalies upon chloral

$$\overbrace{C_4HCl_3O_2}^{\text{Chloral.}} + KO,HO = \overbrace{C_2HCl_3}^{\text{Chloroform.}} + \overbrace{KO,C_2HO_3}^{\text{Formiate potash.}}.$$

5. But it is most economically obtained by acting upon
alcohol with chloride of lime (bleaching powder). Wood
acetone, oil of turpentine, and many essential oils yield it li

der the influence of chloride of lime. Chloroform is readily ocured in a state of purity by the following process:—6 parts of loride of lime, 24 parts of water, and 1 part of alcohol, are to be xed in a capacious still, and the temperature raised as rapidly possible till it reaches 180°. The distillation is then to be ntinued until about one part and a half have passed over; the oducts, consisting chiefly of chloroform accompanied by water, llect in two layers in the receiver—the chloroform constituting e lower layer. It should be decanted from the aqueous portion, d agitated with oil of vitriol in order to destroy traces of volatile ls which accompany it: by another rectification it is obtained in ate of purity.

Chloroform is a colourless, volatile liquid, of high refracting wer. It has a powerful agreeable ethereal odour, and a sweet etrating taste. Alcohol and ether dissolve it in every proportion, it is very sparingly soluble in water. Concentrated sulphuric acid s no action upon it, and even potassium does not occasion its composition. It is inflamed with difficulty, and burns with greenish somewhat smoky flame, producing hydrochloric acid as ell as carbonic acid and water. By admixture with an alcoholic lution of potash it is decomposed, chloride of potassium and miate of potash being produced:—

$$\overbrace{C_2HCl_3}^{\text{Chloroform.}}+4\,(KO,HO)=3\,KCl+\overbrace{KO,C_2HO_3}^{\text{Formiate of potash.}}+2\,H_2O_2.$$

ueous solution of potash does not produce this change, owing the sparing solubility of chloroform in water.

The vapour of chloroform possesses the remarkable power of ducing, in the person who has respired it, complete temporary ensibility to pain. It may be readily inhaled for this purpose placing a small quantity of the liquid upon a sponge or a handrchief which is to be held before the mouth and nostrils. Prof. mpson, of Edinburgh, has the merit of having been the first to ply this property to the alleviation of human suffering; and ce the period when he showed its efficacy for this purpose, it s been extensively employed for rendering patients insensible to in during severe surgical operations.

It is of great importance that the chloroform used for this rpose should be quite pure. In some cases it has been found en exposed to a strong light to have undergone spontaneous composition. It ought to communicate no colour to oil of triol when agitated with it. The liquid itself should be free m colour, and it should be *perfectly destitute* of any chlorous odour. When a few drops are allowed to evaporate on the hand no unpleasant odour should be left.

Chloroform has been regarded as anhydrous formic acid, in which the 3 atoms of oxygen are displaced by 3 of chlorine: but the mode in which it is obtained by substitution from chloride of methyl shows that this cannot be its true constitution; it probably ought to be regarded as the analogue of methylic ether, in which 2 of the atoms of hydrogen are displaced by chlorine; C_2H_3Cl, becoming $C_2\left.\begin{matrix}H\\Cl_2\end{matrix}\right\}Cl$. If distilled in a current of dry chlorine, chloroform is wholly deprived of hydrogen, and yields bichloride of carbon (326), and hydrochloric acid; $C_2\left.\begin{matrix}H\\Cl_2\end{matrix}\right\}Cl + Cl_2 = C_2Cl_4 + HCl$.

Chloroform freely dissolves sulphur, phosphorus, and iodine. It is also a good solvent for fatty and resinous bodies. No other liquid is so perfect a solvent for caoutchouc, which is left unaltered by it on evaporation.

Iodoform (C_2HI_3) is a solid, of a yellow colour, in which 3 atoms of iodine occupy the place of the chlorine in chloroform. A corresponding compound with bromine (C_2HBr_3) may be formed by the distillation of bromide of lime with dilute alcohol. It is a liquid of sp. gr. 2·9, boiling at 305°, and emitting a vapour of a density of 8·632.

§ V. Metallic Derivatives of the Alcohols.

(1024) It has been already stated (989), that when sodium or potassium is made to act upon one of the alcohols, hydrogen is eliminated, and a compound is formed, which presents a certain analogy with the ordinary salts of sodium or of potassium; if we compare the action of sodium upon alcohol, and upon monohydrated acetic acid, the results of the reaction may be thus represented:—

$$2\overbrace{\left(C_4\left.\begin{matrix}H_5\\H\end{matrix}\right\}O_2\right)}^{\text{Alcohol.}} + Na_2 = 2\overbrace{\left(\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2\right)}^{\text{Sodium Alcohol.}} + H_2.$$

$$2\overbrace{\left(\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2\right)}^{\text{Acetic acid.}} + Na_2 = 2\overbrace{\left(\left.\begin{matrix}C_4H_3O_2\\Na\end{matrix}\right\}O_2\right)}^{\text{Acetate of soda.}} + H_2.$$

We have seen that when such compounds are acted upon by the ethers of the hydracids, either simple or double ethers are ed from them by a process of substitution or double decom- ion :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\Na\end{matrix}\right\}O_2}^{\text{Sodium alcohol.}} + \overbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}^{\text{Iodide of ethyl.}} \text{ becoming } \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}} + \overbrace{\left.\begin{matrix}Na\\I\end{matrix}\right\}}^{\text{Iodide of sodium.}}.$$

Within the last few years, however, a series of compounds has obtained in which a metallic element enters still more inti- ly into the composition of the base of the alcohol. The first tance of this class that was carefully investigated was kakodyl H_6As) ; and this body was shown by the masterly researches of en, to perform the part of a compound metal. The subsequent rches of Frankland proved the possibility of obtaining a ber of new bodies more or less analogous to kakodyl ; and the thus opened has since been successfully cultivated by many guished chemists. These investigations have led to the dis- ry of a number of metallic substitution-derivatives of alcohol ch are more or less closely allied to the compound ammonias. e bodies, however, are not all formed upon the type of nia. In some instances each atom of the metal is combined an equivalent of the alcohol radicle, whilst in others 2 equi- ts of the alcohol radicle, in others 3 equivalents, and in some 4 equivalents of the alcohol radicle, are combined with 1 atom e metal.

The most probable explanation of the mode in which these pounds are formed, is that first suggested by Frankland (*Phil.* s., 1852, 440), who regards them as derivatives from the nic compounds of the various metals : and he considers that umber of equivalents of the alcohol radicles which combine any given metal, is regulated by the atomic proportion in h that metal tends to combine with the elements, hydrogen, ur, oxygen, &c. For example :—zinc forms compounds which spond in composition to the oxide of zinc ; and since zinc is tomic, and forms only a single oxide, the methyl and other ol derivatives of zinc contain but a single equivalent of the ol radicle :—

Oxide of Zinc $(ZnO)_2$	;	Zinc-methyl . .	$[Zn,C_2H_3]_2$
		Zinc-ethyl . .	$[Zn,C_4H_5]_2$
		Zinc-amyl. . .	$[Zn,C_{10}H_{11}]_2$

dmium which, like zinc, forms but a single oxide, yields unds of analogous composition, cadmium-ethyl containing $H_5)_2$; and the composition *of magnesium-ethyl* $(Mg,C_4H_5)_2$

is similar. Aluminum forms a sesqui-compound $[Al_2(C_4H_5)_3]$ corresponding to its oxide Al_2O_3.

The tendency of arsenic is to the formation of compounds which contain 2, 3, or 5 atoms of some other element, the bodies thus produced corresponding to realgar, to arseniuretted hydrogen, and to arsenic acid:—

Realgar $(AsS_2)_2$	Kakodyl	$[As,(C_2H_3)_2]_2$
	Arseniodiethyl	$[As,(C_4H_5)_2]_2$
Arseniuretted Hydrogen (AsH_3) Arsenious Acid (AsO_3)	Arseniotriethyl	$As,(C_4H_5)_3$
	Oxide of Kakodyl	$As,(C_2H_3)_2O$
	Chloride of Kakodyl	$As,(C_2H_3)_2Cl$
	Binoxide of Arsenio-monomethyl	As, C_2H_3,O_2
Arsenic Acid (AsO_5)	Chloride of Arsenio-tetrethylium	$As, (C_4H_5)_4,Cl$
	Bichloride of Arsenio-triethyl	$As,(C_4H_5)_3Cl_2$
	Terchloride of Kakodyl	$As,(C_2H_3)_2Cl_3$
	Quadrichloride of Arsenio-monomethyl	As, C_2H_3,Cl_4

Antimony does not form any compound corresponding to realgar, but it yields bodies which contain 3 or 5 atoms of some other element; and the alcohol compounds of this metal correspond to antimoniuretted hydrogen, and to antimonic acid:—

Antimoniuretted Hydrogen (H_3Sb)	Stibiotriethyl	$(C_4H_5)_3Sb$
Antimonic Acid (SbO_5)	Oxide of Stibiotetrethylium	$(C_4H_5)_4Sb,O$
	Oxide of Stibiotriethyl	$(C_4H_5)_3Sb,O_2$

Bismuth presents compounds which correspond to teroxide of bismuth:—

Oxide of Bismuth (BiO_3)	Bistriethyl	$Bi, (C_4H_5)_3$
	Oxide of Bisethyl	$Bi\ [(C_4H_5)O_2]$

Mercury yields compounds corresponding in composition to the red oxide of the metal:—

Red Oxide of Mercury (Hg_2O_2)	Iodide of Hydrargethyl	$Hg_2[(C_4H_5)I]$
	Hydrargodimethyl	$Hg_2(C_2H_3)_2$

Lead yields a compound corresponding to plumbic acid, $2\ PbO_2$:—

Peroxide of Lead $2(PbO_2) = (Pb_2O_4)$	Oxide of Plumbotriethyl (hydrated)	$Pb_2(C_4H_5)_3O,+xHO$
	Plumbodiethyl	$Pb_2(C_4H_5)_4$

The compounds of tin are more numerous, but they are all formed upon one of the three following types, Sn_2O_2, Sn_2O_3, Sn_2O_4, as, for example:—

Sn_2O_2	Stannous Ethide	$Sn_2\left\{\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right.$
Sn_2O_3	Sesquimethide of Tin	$Sn_2\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right.$
	Dimethiodide of Tin	$Sn_2\left\{\begin{matrix}(C_2H_3)_2\\I_2\end{matrix}\right.$
Sn_2O_4	Stannic Ethide	$Sn_2\ (C_4H_5)_4$
	Stannic Ethylomethide	$Sn_2\left\{\begin{matrix}(C_4H_5)_2\\(C_2H_3)_2\end{matrix}\right.$
	Stannic Iodotrimethide	$Sn_2\left\{\begin{matrix}(C_4H_3)_3\\I\end{matrix}\right.$
	Stannic Iododiethide	$Sn_2\left\{\begin{matrix}(C_2H_3)_2\\I_2\end{matrix}\right.$

The compounds of selenium and tellurium with the alcohol radicles are closely allied to the class of bodies which we are now considering, although they present some analogy with the ethers, and they have already been alluded to (999) when speaking of these substances. The intermediate position occupied by selenium and tellurium between the metallic and non-metallic elements, explains why their compounds with the alcohol radicles should exhibit properties intermediate between those of the true ethers and of these metallic derivatives of the alcohols. The tellurium and selenium ethers differ from the ordinary ethers in the tendency to combine with oxygen which they exhibit, thus forming bodies which unite with acids and yield definite salts. Tellurethyl $(C_4H_5Te)_2$, for instance, becomes oxidized and forms the body $(C_4H_5Te)_2O_2$, and this compound, by its combination with oxalic acid, yields a crystalline salt, $2[(C_4H_5Te)_2O_2]C_4O_6+2Aq$.

These *organo-metallic* compounds, as they have been termed, are, as a class, distinguished by the extraordinary energy of their affinities. Their disposition to unite with the electro-negative elements increases with the positive character of the metal, and with the smallness of the atomic weight of the alcohol radicle. Thus, the potassium and sodium compounds are more energetic than those of zinc, and these than the compounds of tin, of lead, or of bismuth; and the methylic compounds of each metal are more active than the ethylic, and these again than the amylic compounds.

Many of the compounds of the alcohol radicles with the metals, such for example as zinc-methyl, kakodyl, stibiotriethyl, and bistriethyl, have an affinity for oxygen so powerful that they take fire by simple contact with it, or with atmospheric air: but it is important to remark, that the results of such oxidation are very different in different cases. In some instances, when the operation is conducted slowly and with due care, organo-metallic oxides are procured, into the composition of which the alcohol radicle enters;

they thus furnish bases which, like oxide of kakodyl, combine with acids, neutralizing them and forming well-defined crystallizable compounds. In other instances no such basic organo-metallic oxides can be obtained: thus zinc-methyl and zinc-ethyl, although their affinity for oxygen is very intense, do not yield any organo-metallic base by the gradual action of oxygen upon them.

Kakodyl and arseniodiethyl (the kakodyl of the ethylic series), both unite with oxygen in two proportions: the lower oxide with one atom of oxygen, in the case of kakodyl, exerting the properties of a powerful base, neutralizing acids, and forming with them crystallizable salts; whilst with the three atoms of oxygen a strong monobasic acid is produced; thus:—

Kakodyl . . .	$[As(C_2H_3)_2]_2$.
Oxide of kakodyl . .	$[As(C_2H_3)_2O]_2$.
Kakodylic acid . .	$HO,As(C_2H_3)_2O_3$.

Frankland accounts for the difference between the results of the oxidation of kakodyl and of zinc-methyl from the circumstance that in the case of oxide of zinc no binoxide is known, and as zinc-methyl is formed upon the type of oxide of zinc, there should therefore be no tendency to the formation of an oxide of zinc-methyl. In the case of kakodyl, the addition of an atom of oxygen produces a compound corresponding in a certain degree with arsenious acid:—

$$As\left\{\begin{matrix}O\\O\\O\end{matrix}\right., \text{ Arsenious acid}; \qquad As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\end{matrix}\right., \text{ Oxide of kakodyl};$$

whilst kakodylic acid corresponds to arsenic acid:—

$$As\left\{\begin{matrix}O\\O\\O\\O\\O\end{matrix}\right., \text{ Arsenic acid}; \qquad As\left\{\begin{matrix}C_2H_3\\C_2H_3\\O\\O\\O\end{matrix}\right., \text{ Kakodylic acid}.$$

The organo-metallic compounds, to use Frankland's words, when "in a state of partial saturation, play the part of compound radicles: they are uniatomic, biatomic, teratomic, or quadratomic, according to the number of molecules requisite to complete their saturation. On the other hand, organo-metallic bodies, in a state of saturation, never perform radical functions; they never undergo chemical change without decomposition." (See *Q. J. Chem. Soc.*, xiii. 192, which contains a recent digest, by Frankland, of the principal facts bearing upon this subject.)

This view is ingenious; indeed it contains the germ of the ry of polybasic elements (922). Frankland has recently sup- ed it by researches which seem to show that a basic organic le, such as methyl or ethyl, can be substituted for oxygen, h is strongly electro-negative. Thus he has obtained a *dini- hylic acid* $[N_2(C_4H_5)O_3]$, derived from 2 atoms of deutoxide trogen 2 (NO_2), in which 1 atom of oxygen has been dis- d by ethyl; and *ethylotrithionic acid* $[S_6(C_4H_5)_2O_{10}]$ may be ded as formed from 3 molecules of sulphurous acid (S_2O_4), ich 2 atoms of the oxygen have been displaced by ethyl. e bodies are produced by the action of zinc-ethyl upon deut- of nitrogen and sulphurous acid respectively (*Proceed. Roy.* viii. 198).*

Organo-metallic compounds may be formed by various pro- s, the most important of which are the following:—

1. Combination of the organic radicle in the nascent state the metal, as in the preparation of magnesium ethyl:—

$$2\,\overbrace{\left(\begin{matrix}C_4H_5\\ I\end{matrix}\right\}}^{\text{Iodide ethyl.}}+2\,Mg_2=2\left(\begin{matrix}Mg\\ I\end{matrix}\right\}+\overbrace{Mg_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.}^{\text{Magnesium ethyl.}}$$

2. Decomposition of the iodides of the alcohol radicles by an y of the metal with potassium or sodium, as when stannous le is formed by the action of stannide of sodium on iodide of thyl:—

---

* *Boric Ethide* or *Borotriethyl*, $B(C_4H_5)_3$, *Sp. Gr. of Liquid* 0·696; *of* ur 3·4; *Boiling point* 194°.—Frankland and Duppa have recently d. *Roy. Soc.* x. 568) obtained an interesting addition to this class of s in a compound corresponding to boracic acid, in which the three atoms ygen are displaced by ethyl. It is a colourless liquid which takes fire spon- ously when exposed to the air, and burns with a beautiful green flame. It is formed by decomposing boracic ether by means of zinc-ethyl, and is d by distillation from the accompanying ethylate of zinc and unaltered -ethyl:—

$$2\,\overbrace{(3\,C_4H_5O,BO_3)}^{\text{Boracic ether.}}+3\,\overbrace{Zn_2(C_4H_5)_2}^{\text{Zinc-ethyl.}}=2\,\overbrace{[B(C_4H_5)_3]}^{\text{Boric ethide.}}+\overbrace{6\,Zn_2C_4H_5O_2}^{\text{Ethylate of zinc.}}.$$

If allowed to oxidize slowly by the gradual admission of air into a flask, it s a colourless liquid $[B(C_4H_5)_3O_4]$ which is decomposed by distillation. body is immediately dissolved by water, and is converted into alcohol, a white volatile crystallized compound with an intensely sweet taste:—

$$B(C_4H_5)_3O_4+2\,H_2O_2=B,C_4H_5,H_2O_4+2\,C_4H_6O_2.$$

The anomalous oxidized body $B(C_4H_5)_3O_4$, is regarded by Frankland as $\left(\begin{matrix}C_4H_5\\(C_4H_5)_2O_2\end{matrix}\right.$, or *boric dioxyethide.* Its composition, however, does not agree the theory of these bodies given above: for no oxidized body of this sition is known, but it seems rather to point to the existence of a class of compounds which contain 5 atoms of oxygen, or other element, cor- ding to nitric, chloric, and arsenic acid.

$$2\,\overbrace{\left(\begin{matrix}C_2H_3\\ I\end{matrix}\right\}}^{\text{Iodide ethyl.}} + \overbrace{Sn\left\{\begin{matrix}Na\\ Na\end{matrix}\right.}^{\text{Stann. sodium.}} = 2\left(\begin{matrix}Na\\ I\end{matrix}\right\} + \overbrace{Sn\left\{\begin{matrix}C_2H_3\\ C_2H_3\end{matrix}\right.}^{\text{Stann.-ethyl.}}$$

3. Action of organo-zinc compounds upon the haloid compounds of the metals, as in the preparation of hydrargo-methyl by the action of zinc-methyl upon corrosive sublimate :—

$$\overbrace{Zn_2\left\{\begin{matrix}C_2H_3\\ C_2H_3\end{matrix}\right.}^{\text{Zinc-methyl.}} + \overbrace{Hg_2\left\{\begin{matrix}Cl\\ Cl\end{matrix}\right.}^{\text{Cor. sublim.}} = \overbrace{Hg_2\left\{\begin{matrix}C_2H_3\\ C_2H_3\end{matrix}\right.}^{\text{Hydrargo-methyl.}} + Zn_2\left\{\begin{matrix}Cl\\ Cl\end{matrix}\right.$$

4. Displacement of the metal in the organo-metallic compound by another more positive metal, as when sodium-ethyl is formed from zinc-ethyl by the action of sodium upon the zinc compound :—

$$3\left(Zn_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.\right) + Na_2 = \overbrace{\left[2\left(Zn_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.\right) + Na_2\left\{\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right.\right]}^{\text{Compound of sodium-ethyl with zinc-ethyl.}} + Zn_2.$$

In order to illustrate the properties and mode of formation of these singular compounds, a description will now be given of a few of the organo-metallic bodies into the formation of which zinc, arsenic, and antimony enter.

(*a*) *Compounds of Zinc with the Alcohol Radicles.*

(1025) The properties of the compounds formed by zinc with the alcohol radicles are very remarkable, and these substances are further interesting in connexion with the process of isolating the alcohol radicles themselves.

ZINC-METHYL [$(C_2H_3,Zn)_2=95{\cdot}5$; *Comb. Vol.* 4] is a very volatile, colourless, transparent, and highly mobile liquid, with a penetrating, peculiar, and insupportable odour. It is immediately decomposed by oxygen, chlorine, and iodine, forming compounds which are rather unstable. If placed in contact with atmospheric air, it takes fire instantaneously, burning with a beautiful greenish-blue flame, and forming white clouds of oxide of zinc ; in contact with pure oxygen it burns with explosion, and the presence of a small quantity of its vapour in combustible gases gives them the property of spontaneous inflammability on admixture with oxygen. When thrown into water, zinc-methyl decomposes this liquid with explosive violence, attended with flame; and if the reaction be moderated, so as to prevent any intense elevation of temperature, the sole products of the decomposition are oxide of zinc and hydride of methyl (marsh gas); $(C_2H_3,Zn)_2 + H_2O_2 = 2\,(C_2H_3,H) + Zn_2O_2$.

Frankland has shown that, owing to the intense affinity of zinc-methyl for oxygen and chlorine, it is possible in certain cases to employ it for effecting the substitution of methyl for oxygen and for chlorine.

In order to obtain zinc-methyl in a state of purity, iodide of methyl is sealed up, with an excess of dry granulated zinc, in a strong glass tube, drawn out to a capillary end, and exposed to a temperature of from 300° to 320° in an oil-bath, until all the iodide of methyl has disappeared. A mass of white crystals, consisting of a compound of zinc-methyl with iodide of zinc, and a colourless, mobile liquid, which is zinc-methyl, are thus formed, and at the same time a considerable quantity of gaseous methyl is produced and confined. One portion of the iodide of methyl is converted into iodide of zinc and methyl,

$$2\,\overbrace{(C_2H_3I)}^{\text{Iodide of methyl.}} + 2\,Zn = \overbrace{(C_2H_3,C_2H_3)}^{\text{Methyl.}} + 2\,ZnI,$$

whilst another portion yields iodide of zinc and zinc-methyl,

$$2\,\overbrace{(C_2H_3I)}^{\text{Iodide of methyl.}} + 2\,ZnZn = \overbrace{(C_2H_3,Zn)_2}^{\text{Zinc-methyl.}} + 2\,ZnI.$$

The zinc-methyl may be obtained by breaking off the capillary extremity, and allowing the included gaseous methyl to escape, and the liquid contents are separated from the solid ones by distillation at a gentle heat in an atmosphere of dry hydrogen.

(1026) ZINC-ETHYL $(C_4H_5,Zn)_2 = 123{\cdot}5$: *Sp. gr. of vapour* 4·259; *of liquid* 1·182 at 64°; *Boiling pt.* 244°. (Frankland, *Phil. Trans.* 1855.)—This compound is a colourless, transparent, mobile liquid, which refracts light strongly, and is possessed of a peculiar powerful, but not disagreeable odour. It is not solidified by a cold of −8°. It may be distilled without change in vessels filled with carbonic acid, or with hydrogen. Zinc-ethyl is less inflammable than zinc-methyl, but its affinity for oxygen is sufficiently intense to cause it to take fire as soon as the liquid is brought into contact with that gas, or with atmospheric air, when it burns with a brilliant blue flame, fringed with green, and forms dense white clouds of oxide of zinc. If a cold piece of glass, or of porcelain, be held in the flame, it becomes coated with a deposit of metallic zinc, surrounded by a white ring of the oxide of this metal. If the oxidation be allowed to take place more slowly, zinc-alcohol (C_4H_5O,ZnO) (or ethylate of zinc) is the principal product; and this mode of the formation of zinc-alcohol by the direct combination of zinc-ethyl with oxygen, is certainly very remarkable. Water immediately decomposes zinc-ethyl; oxide of zinc, and the gaseous hydride of ethyl (C_4H_5,H), being the result:—

$$(C_4H_5Zn)_2 + H_2O_2 = 2\ (C_4H_5H) + Zn_2O_2.$$

Iodine, bromine, and chlorine, decompose zinc-ethyl with great violence; if the action be moderated, iodide, bromide, or chloride of zinc is formed, whilst the corresponding compound of ethyl with the halogen is produced; in the case of iodine, the reaction may be thus represented:—

$$(C_4H_5Zn)_2 + 2\ I_2 = 2(C_4H_5I) + 2\ ZnI.$$

A similar effect is produced if zinc-ethyl be heated with powdered sulphur, the double sulphide of zinc and ethyl being formed.

Preparation.—Zinc-ethyl is obtained by heating anhydrous iodide of ethyl, diluted with an equal volume of anhydrous ether* (to regulate the reaction) with twice its weight of well-dried granulated zinc. The mixture is introduced into a sealed glass tube, and heated in a digester to about 266° for twelve or eighteen hours. When large quantities are required, the safest plan is to conduct the operation in a strong metallic vessel, or species of digester. A full description of this apparatus is given by Frankland in his paper.† If the materials employed for the preparation of the zinc-ethyl are really anhydrous, very little permanent gas is produced, but if moisture be present, a quantity of hydride of ethyl is formed. After the apparatus has become cool, the permanent gas, if any, is allowed to escape; and the zinc-ethyl is distilled from the materials employed in its preparation, in vessels filled with carbonic acid or hydrogen. Particular modes of manipulation are required during the distillation and purification of the product, in order to prevent the access of air, which would oxidize and destroy the compound. For details upon these points, the reader is referred to the memoir already cited.

(1027) Wanklyn found that if a piece of sodium be sealed up in a tube (previously filled with coal gas) with about 10 times its weight of zinc-ethyl, in the course of a few days the sodium is dissolved, a deposit of metallic zinc takes place, and a viscid liquid is formed:—

---

* In order to deprive this mixture completely of moisture, it is agitated with about one-twentieth of its weight of anhydrous phosphoric acid.

† Pebal, however, conducts the operation in ordinary glass retorts filled with carbonic acid gas.

$$3\left(\begin{array}{c}\mathrm{Zn_2}\\(\mathrm{C_4H_5})_2\end{array}\right\}+\left.\begin{array}{c}\mathrm{Na}\\\mathrm{Na}\end{array}\right\}=\left.\begin{array}{c}\mathrm{Na_2}\\(\mathrm{C_4H_5})_2\end{array}\right\}+2\left.\begin{array}{c}\mathrm{Zn_2}\\(\mathrm{C_4H_5})_2\end{array}\right\}+\left.\begin{array}{c}\mathrm{Zn}\\\mathrm{Zn}\end{array}\right\}.$$

liquid consists of a solution of a compound of sodium-
d zinc-ethyl [$Na_2(C_4H_5)_2 + 2\,Zn_2(C_4H_5)_2$], dissolved in an
f zinc-ethyl, and when exposed to a temperature of 32°
l crystals of this compound are deposited; they fuse at
°. Attempts to procure sodium-ethyl in an isolated state
nsuccessful. When the foregoing double compound is
n evolution of gas occurs, and an alloy of sodium and zinc,
n carbonaceous residue, is left. When exposed to the
crystals instantly take fire, burning explosively with a
ame. Water decomposes them with evolution of pure
of ethyl. The reaction with carbonic acid is especially
ble, propionate of soda being formed, which combines with
-ethyl, and may be obtained in a separate form by decom-
he compound with water. The reaction which gives rise
ormation of propionic acid appears to be the following:—

$$O_4+\overbrace{\mathrm{Na\,C_4H_5,\ 2\,Zn\,C_4H_5}}=\overbrace{\mathrm{NaO,C_6H_5O_3}}^{\text{Propionate of soda.}}+\overbrace{(\mathrm{ZnC_4H_5})_2}^{\text{Zinc-ethyl.}}.$$

reaction is extremely interesting, since it points out a
of forming the fatty acids by substitution from carbonic
Sodium-methyl has been found in like manner to yield
of soda, and sodium-amyl would probably furnish caproate
. It is remarkable that a series of monobasic acids are
tained from the dibasic carbonic acid.

compound of zinc-ethyl with potassium-ethyl may be
d by means analogous to those adopted for procuring the
compound; and there can be no doubt that corresponding
nds of the other alcohol radicles could be procured.

28) *Zinc-amyl* $(C_{10}H_{11}Zn)_2$.—This body is obtained by de-
ing iodide of amyl with zinc in a sealed tube, at a tempera-
356°. It forms a colourless, transparent liquid, which emits
and rapidly absorbs oxygen when exposed to the air; but
not take fire spontaneously. Water decomposes it into
f zinc and hydride of amyl:—

$$Zn_2(C_{10}H_{11})_2 + H_2O_2 = 2\,C_{10}H_{11}H + Zn_2O_2.$$

(b) *Compounds of Arsenic with the Alcohol Radicles.*

forms with the alcohol radicles three classes of com-
h have been minutely examined in the methyl and in
ries:—

1. Arseniodimethyl or kakodyl .	$(C_4H_6As)_2 = [(C_2H_3)_2As]_2$	Arseniodiethyl (ethylic kakodyl)	$(C_8H_{10}As)_2$
2. Arseniotrimethyl	$C_6H_9As = [(C_2H_3)_3As]$	Arseniotriethyl .	$C_{12}H_{15}As$
3. Oxide of Arsenio-tetramethylium	$C_8H_{12}As,O = (C_2H_3)_4As,O$	Oxide of Arsenio-tetrethylium .	$C_{16}H_{20}As,O$

(1029) Kakodyl; *Arseniodimethyl* $[(C_2H_3)_2As]_2$ or =210; *Comb. vol.* 4; *Sp. gr. of vapour* 7·1.—This b isolated form is more properly regarded as kakodylide o It is an extremely poisonous, colourless, viscous liqui than water; it emits fumes, and takes fire spontaneo exposed to the air. Its vapours have a disgustin odour. The boiling point of kakodyl is about 338°; becomes solid and crystallizes in square prisms. It is o soluble in water, but is readily dissolved by alcohol an When heated to about 750° it is entirely decomposed in arsenic and a gaseous mixture consisting of 2 volume gas and 1 volume of olefiant gas:—

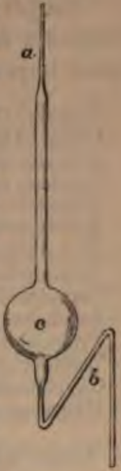
$$\overbrace{(C_4H_6As)_2}^{\text{Kakodyl.}} = As_2 + 2\,\overbrace{C_2H_4}^{\text{Marsh gas.}} + \overbrace{C_4H_4}^{\text{Olefiant gas.}}.$$

Kakodyl burns in oxygen with a pale blue flame, produc with carbonic and arsenious acids: but if atmosphe admitted bubble by bubble into kakodyl, white fumes a and oxide of kakodyl $[(C_4H_6As)O]_2$ is the result: an oxygen converts it into kakodylic acid $(C_4H_6As)O_3$; supply of oxygen be insufficient to complete this chang late of kakodyl $(C_4H_6As)O$, $(C_4H_6As)O_3$ (binoxide of k produced.

The remarkable peculiarity of kakodyl is its pow uniting directly with oxygen; and it exhibits a similar to combine with sulphur, chlorine, &c.; in this mann forms the part of a simple metallic body, since the grou (which may be represented by the abbreviated symbol K of being substituted for hydrogen. The discovery of pound in an isolated form exercised an important influ the development of the theory of organic chemistry, as it the first instance of what was then regarded as the isola organo-metallic basyl; although other bodies more or l gous to it in this respect are now known. Most chem ever, have now agreed to double the formula for kakody it loses its importance as a radicle, the progress of resear rendered it probable that all the compounds formerly isolated radicles are combinations of those radicles with t (918).

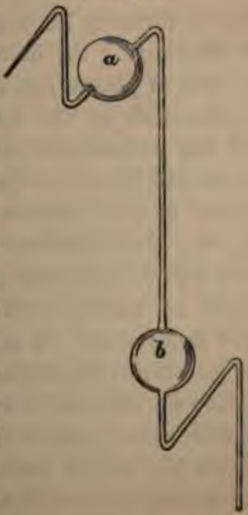
lyl was obtained by Bunsen from its chloride, which, ted with fragments of granulated zinc, is decomposed; f zinc being formed, whilst pure kakodyl is liberated. de employed for this purpose must be quite anhydrous, from oxide of kakodyl. After digestion entrated hydrochloric acid, the chloride is stand for several days upon fragments of and chloride of calcium. This purification oride must be effected in a bulb-tube of the vn in fig. 361, the quicklime and chloride being first introduced into the bulb.

FIG. 361.



a view to avoid the contact of air with the aterial, a current of dry carbonic acid gas is by the fine tube *a*, in order to displace the ic air completely, and the capillary tubes sealed: when the chloride of kakodyl is to uced, the point of the capillary tube *a* is cut y means of a caoutchouc tube it is connected nd syringe; the tube *b* is then opened, and dip into the liquid chloride, which by the t of the piston is drawn into the bulb. The ition must be effected in an apparatus similar hown in fig. 362. The zinc having first been placed in *a*, the apparatus is to be filled bonic acid, and a portion of the of kakodyl is admitted. The ca- ubes are then sealed, and heat is to the bulb *a*, which acts as a serving as the receiver. The zinc becomes dissolved without any of gas; when the action has he apparatus is allowed to cool, apillary tube at *b* is opened under ater: the bulb is then heated expel a portion of the carbonic d water enters as the apparatus ter which the capillary tube is aled: by inclining the tube, the made to act upon the crystallized bulb *a*; it thus dissolves the ic, leaving the excess of metallic rating kakodylide of kakodyl f an oily fluid, which is *transferred to* a bulb-tube

FIG. 362.



of the form of fig. 361, the bulb having been previous
chloride of calcium, and the air displaced by means
acid, in the manner already described : here it is dried
ferred to the bulb apparatus (fig. 362), and rectified
portion of zinc. Kakodyl may also be obtained by
mercury upon sulphide of kakodyl.

(1030) *Compounds derived from Kakodyl.*—Bur
scribed a large number of compounds of kakodyl;
more important are the following;—

Kakodyl (kakodylide of kakodyl)	$(C_4H_6As)_2$
Oxide of kakodyl	$[(C_4H_6As)O]_2$
Binoxide of kakodyl (kakodylate of kakodyl)	$(C_4H_6As)O,($
Sulphate of kakodyl	$[(C_4H_6As)O]_2$
Kakodylic acid	$HO,(C_4H_6A$
Kakodylate of silver	$AgO,(C_4H_6A$
Protosulphide of kakodyl	$[(C_4H_6As)S]_2$
Bisulphide of kakodyl.	$(C_4H_6As)S,(C$
Tersulphide of kakodyl (sulphokakodylic acid)	$(C_4H_6As)S_3$
Sulphokakodylate of silver	$AgS,(C_4H_6A$
Protochloride of kakodyl	$(C_4H_6As)Cl$
Terchloride of kakodyl	$(C_4H_6As)Cl_3$
Oxychloride of kakodyl	$(C_4H_6As)O, 3$
Hydrargo-oxychloride of kakodyl. . . .	$(C_4H_6AsO)_2.$

Oxide of Kakodyl $(C_4H_6As, O)_2$: *Sp. gr. of vapou*
preparation of the compounds of kakodyl, owing to t
bility of many of them, and their highly poisonous
both difficult and dangerous. Oxide of kakodyl i
form constitutes the horribly fœtid, spontaneously
liquid, formerly known as *Cadet's fuming liquor*, or *al*
is obtained by the distillation of a mixture of equal
acetate of potash and arsenious acid. The receiver
to the neck of the retort, and furnished with a tube
off the gaseous products into the chimney; the reto
be heated by a sand bath, the temperature of which
raised to dull redness. The distilled liquid separate
layers; the lower one consists of arsenic; above thi
oily liquid, composed chiefly of a mixture of impure
oxide of kakodyl; and above this is a mixture of w
and acetic acid. A copious disengagement of carbo
of marsh gas accompanies the operation. The stratu
(oxide of kakodyl) is drawn off, by means of a syph
boiled water, into a flask also filled with the same
which the longer limb of the syphon is plunged w
preventing the contact of the air with the inflamma
It is washed with boiled water, and then rectified fro
potash in a current of hydrogen; air is then gradu

distillate, sufficiently slowly to prevent it from taking fire.
uid thus obtained consists of a mixture of the oxide of
l and kakodylic acid; it is dissolved in water and distilled.
a quantity of water having the odour of kakodyl passes
nd when the temperature rises to 248°, the oily liquid
istils is nearly pure oxide of kakodyl. A second rectifica-
m caustic baryta in vessels from which air is excluded,
s the compound in a state of purity. All these opera-
ust be conducted with the greatest possible care, and with
ption of special precautions, on account of the deadly
f the vapours. Full particulars upon all these points are
y Bunsen in the interesting and remarkable series of
which he has published upon the compounds of kakodyl
derivatives. These papers are worthy of careful study, as
of ingenuity and precision in the prosecution of a research
ith unusual difficulty and danger (Liebig's *Annal.*, xxxvii.
14; and xlvi. 1). Oxide of kakodyl is a colourless,
ethereal liquid, endowed with a penetrating odour, and
at about 248°; it is insoluble in water, but soluble in
. It slowly absorbs oxygen from the air, and combines
ids to form salts: the sulphate crystallizes in radiating
needles.

ide of kakodyl also combines with the electro-negative
es with facility. If an alcoholic solution of corrosive sub-
be mixed with a dilute solution of Cadet's liquor in alcohol,
ndant white precipitate is formed, and the intolerable odour
odyl disappears completely. The precipitate if collected,
to remove the adhering mother-liquor, and redissolved in
water, is deposited in well defined crystals $(C_4H_6AsO)_2$,
l. The ready formation of this crystalline compound
ne of the best means of purifying the crude compounds of
yl. When this mercurial compound is distilled with con-
ted hydrochloric acid it furnishes *chloride of kakodyl*
As)Cl; *Sp. gr. of vapour* 4·56] in the form of a colourless
which boils at about 212°, and remains liquid at a tempera-
—49°. It takes fire spontaneously in the air, and in an
here of chlorine; in the latter case depositing carbon
ntly. Its vapour is still more deleterious than that of the
chloride of kakodyl is insoluble in water and in ether, but
luble in alcohol. *Iodide* and *bromide of kakodyl* may be
d by treating the mercurial compound with hydriodic or
bromic acid.

of kakodyl $(C_4H_6As, C_2N$; *or KdCy) Sp. gr. of vapour*

4·63; *Boilingpt.* 284°.—This compound shows a remarkable tendency to crystallization; it appears to be the most deadly compound of the whole series, a single grain diffused in vapour through a room being sufficient to produce numbness of the hands and feet, vertigo, and even syncope, in those exposed to its effects. It may be obtained in brilliant prisms which fuse at 91°, by decomposing a concentrated solution of cyanide of mercury with oxide of kakodyl, and rectifying the crystals over caustic baryta.

Sulphur combines with kakodyl in three proportions; the *protosulphide of kakodyl* $(KdS)_2$ is a colourless, very fœtid liquid, which absorbs oxygen rapidly from the air. Its boiling point is above 212°, and it emits a vapour of sp. gr. 7·81. It is readily soluble in alcohol and in ether: it combines easily with an additional quantity of sulphur, and becomes converted into the solid *bisulphide* $(KdS_2)_2$. The *tersulphide* (KdS_3) possesses the properties of a sulphur acid. If an alcoholic solution of the protosulphide be mixed with an alcoholic solution of nitrate of copper, octohedral crystals of adamantine lustre are deposited; they are permanent in the air, and consist of a double sulphide of kakodyl and copper (C_4H_6AsS, CuS). The protosulphide of kakodyl may be obtained by distilling Cadet's liquor with sulphide of barium.

Kakodylic acid (HO, C_4H_6As, O_3) crystallizes in oblique equilateral prisms which are soluble in water and in alcohol. It is remarkable that it appears to possess little or no poisonous action upon the animal system, seven grains of it having been injected into the blood of a rabbit without producing any marked effect. It is a weak acid, and decomposes the carbonates slowly. Its salts, with the exception of the silver salt, crystallize with difficulty. The acid is easily obtained by treating oxide of kakodyl with red oxide of mercury: metallic mercury is reduced, whilst the acid is dissolved.

(1031) ARSENIODIETHYL $(C_8H_{10}As)_2=[(C_4H_5)_2As]_2$ forms a series of compounds parallel to those of kakodyl, but it does not so instantaneously burst into flame on exposure to air, and, generally, its affinities are somewhat less powerful.

(1032) ARSENIOTRIMETHYL $[(C_2H_3)_3As]$ corresponds in composition with the analogous compound of the ethyl series, which has been more completely examined.

ARSENIOTRIETHYL $[(C_{12}H_{15}As)=(C_4H_5)_3As]$; *Sp. gr. of liquid* 1·151; *of vapour* 5·278.—This is a fuming, colourless, mobile liquid, of high refracting power, with the oppressive odour of arseniuretted hydrogen. It is soluble in alcohol and in ether, but n water. It begins to boil at 284° ; but it undergoes partial omposition during distillation. It does not usually take fire exposure to the air unless gently heated, though it rapidly rbs oxygen. It also becomes gradually oxidized if its solu- in ether be exposed to the air ; and it then produces a base, $H_5)_3As\,O_2]$, which requires two atoms of a monobasic acid for aturation. A sulphide, chloride, and iodide may be obtained, of which contains two atoms of the electro-negative body to f arseniotriethyl ; the iodide having the formula $(C_4H_5)_3As, I_2$. niotriethyl is obtained by the action of iodide of ethyl upon an of arsenic and sodium ; under these circumstances it is accom- d by arseniodiethyl, from which it is separated by distillation ; atter compound being the less volatile, remains in the retort. e operations must be performed in vessels filled with carbonic gas. The compounds of arseniotriethyl have the closest analogy those of stibiotriethyl (1035).

(1033) OXIDE OF ARSENIOTETRETHYLIUM $[(C_4H_5)_4As, O], HO$. arseniotriethyl be treated with iodide of ethyl, it combines with forms a new compound, which has been termed iodide of tetrethylium $[(C_4H_5)_4As, I]$. It may be crystallized from or from alcohol, and when its aqueous solution is treated xide of silver, iodide of silver is formed, while the oxide of tetrethylium is obtained in solution. It may be procured form of a white hydrated solid by evaporation *in vacuo*, and the ordinary ammonium bases, it presents the properties of a ful and caustic alkali. It forms crystallizable salts, which eutral contain 1 atom of a monobasic acid.

y treating kakodyl with iodide of ethyl, an *iodide of arseniodi- ethylium* $[(C_4H_5)_2(C_2H_3)_2AsI]$ is formed ; from which the rated oxide $[(C_4H_5)_2(C_2H_3)_2AsO]HO$, may be obtained by the of oxide of silver. A corresponding compound containing $[(C_{10}H_{11})_2(C_2H_3)_2AsI]$ may be obtained by substituting iodide yl for iodide of ethyl when acting upon kakodyl. The attempts late the unoxidized compound metals of the form of arsenio- thylium $[(C_4H_5)_4As]$ have as yet been fruitless.

(c) *Compounds of Antimony with the Alcohol Radicles.*

(1034) The alcohol derivatives of antimony have been carefully ed by Löwig and Schweizer (Liebig's *Annalen*, lxxv. 315), by Landolt (*Ib.* lxxviii. 91, and lxxxiv. 44). No compounds mony corresponding to the kakodyl series have been dis- d, but those analogous to the second and third class of the in water. It begins to boil at 284°; but it undergoes partial mposition during distillation. It does not usually take fire exposure to the air unless gently heated, though it rapidly rbs oxygen. It also becomes gradually oxidized if its solu- in ether be exposed to the air; and it then produces a base, $H_5)_3AsO_2]$, which requires two atoms of a monobasic acid for turation. A sulphide, chloride, and iodide may be obtained, of which contains two atoms of the electro-negative body to f arseniotriethyl; the iodide having the formula $(C_4H_5)_3As, I_2$. iotriethyl is obtained by the action of iodide of ethyl upon an of arsenic and sodium; under these circumstances it is accom- d by arseniodiethyl, from which it is separated by distillation; tter compound being the less volatile, remains in the retort. e operations must be performed in vessels filled with carbonic gas. The compounds of arseniotriethyl have the closest analogy those of stibiotriethyl (1035).

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(c) *Compounds of Antimony with the Alcohol Radicles.*

(1034) The alcohol derivatives of antimony have been carefully ned by Löwig and Schweizer (Liebig's *Annalen*, lxxv. 315), by Landolt (*Ib.* lxxviii. 91, and lxxix. 44). No compounds ntimony corresponding to the kakodyl series have been dis- red; but those analogous to the second and third class of the arsenical compounds have been studied. The following principal compounds with methyl and with ethyl which cor to the second series of the arsenical compounds :—

Stibiotrimethyl . . .	C_6H_9Sb	$=(C_2H_3)_3Sb$
Oxide of stibiotrimethyl	C_6H_9Sb,O_2	$=(C_2H_3)_3Sb,O_2$
Sulphide ,,	C_6H_9Sb,S_2	$=(C_2H_3)_3Sb,S_2$
Chloride ,,	C_6H_9Sb,Cl_2	$=(C_2H_3)_3Sb,Cl_2$
Sulphate ,,	$C_6H_9Sb,O_2,\ S_2O_6$	$=(C_2H_3)_3Sb,O_2,$
Nitrate ,,	$C_6H_9Sb,O_2,\ 2\ NO_5$	$=(C_2H_3)_3Sb,O_2,$

Stibiotriethyl	$C_{12}H_{15}Sb$	$=(C_4H_5)_3Sb$
Oxide of stibiotriethyl .	$C_{12}H_{15}Sb,O_2$	$=(C_4H_5)_3Sb,O_2$
Sulphide ,,	$C_{12}H_{15}Sb,S_2$	$=(C_4H_5)_3Sb,S_2$
Chloride ,,	$C_{12}H_{15}Sb,Cl_2$	$=(C_4H_5)_3Sb,Cl_2$
Sulphate ,,	$C_{12}H_{15}Sb,O_2,\ S_2O_6$	$=(C_4H_5)_3Sb,O_2,$
Nitrate ,,	$C_{12}H_{15}Sb,O_2,\ 2\ NO_5$	$=(C_4H_5)_3Sb,O_2,$

The radicles stibiotrimethyl and stibiotriethyl at t glance seem to resemble ammonia in composition, since t respond to antimoniuretted hydrogen in which the three hydrogen have been displaced by methyl or by ethyl, b entirely differ from ammonia in their mode of combinatio of these bodies forms an oxide with two atoms of oxyg this oxide requires two equivalents of hydrochloric or acid for its saturation. Frankland views stibiotriethyl as presentative of the oxide of antimony (SbO_3), in which t atoms of oxygen have been displaced by an equal number o lents of ethyl ; the binoxide of stibiotriethyl representing a acid (SbO_3, O_2). A similar explanation may be applie corresponding compounds of arsenic, arseniotriethyl and i

Antimony also forms a second class of organo-meta pounds, the methyl series of which is represented as follo

Oxide of stibiotetramethylium	$C_8H_{12}SbO =$	$(C_2H_3)_4SbO$
Sulphide ,,	$C_8H_{12}SbS =$	$(C_2H_3)_4SbS$
Chloride ,,	$C_8H_{12}SbCl =$	$(C_2H_3)_4SbCl$
Sulphate ,,		$2\,[(C_2H_3)_4SbO]S_2$
Bisulphate ,,		$(C_2H_3)_4SbO,HO$
Nitrate ,,		$(C_2H_3)_4SbO,NO$

This group appears to correspond exactly with the an series, with which indeed it presents the most striking an

(1035) STIBETHYL, or *Stibiotriethyl* [$(C_4H_5)_3Sb$] : *liquid* 1·324 ; *of vapour*(=4 vols.) 7·438 ; *Boiling pt.* 3 order to procure stibiotriethyl, an alloy of antimony wi sium must be prepared by heating a mixture of 4 parts dered antimony and 5 of crude tartar in a covered crucibl alloy, after being reduced to powder, is to be mixed w es its weight of siliceous sand, and placed in a retort with iodide ethyl. The operation must be conducted upon small quantities a time, and in an atmosphere of carbonic acid: it requires a mber of minute precautions (Lowig and Schweizer, *loc. cit.*). biotriethyl is a heavy, limpid liquid, with an insupportable odour onions. It is insoluble in water, but very soluble in alcohol l in ether. When a glass rod is dipped into pure stibiotriethyl l exposed to the air, the liquid emits dense white fumes, and es fire in a few moments, burning with a white luminous flame.

Stibiotriethyl decomposes concentrated hydrochloric acid; rogen being liberated, whilst bichloride of stibiotriethyl is ned as a heavy insoluble oil.

The *binoxide* is obtained by acting on stibiotriethyl with red de of mercury. It forms a viscous transparent liquid, soluble water and in alcohol. The solution has a very bitter taste, but oes not appear to be poisonous. It is not volatile, and forms s which crystallize with difficulty, except the nitrate, which us beautiful rhomboidal, readily soluble crystals, which melt at ° into a colourless liquid, and are decomposed with deflagration raising the heat.

Bisulphide of Stibiotriethyl [$(C_4H_5)_3$ Sb, S_2].—If stibiotriethyl sulphur be mixed under water, they enter directly into comation, and great heat is evolved during the reaction: the comd is soluble in water, and may be obtained in crystals on ration. This solution when mixed with solutions of the llic salts precipitates the metallic sulphides (just as sulphide potassium would do,) while a salt of oxide of stibiotriethyl ns dissolved:—for instance, if sulphate of copper be mixed a solution of sulphide of stibiotriethyl, sulphate of stibiotrihyl and sulphide of copper are formed:—

$$(C_4H_5)_3\ Sb,\ S_2 + 2\ CuO,\ S_2O_6 = 2\ CuS + (C_4H_5)_3\ SbO_2,\ S_2O_6.$$

Biniodide of Stibiotriethyl is soluble in alcohol, from which it stallizes in long transparent colourless needles. It is also ble in ether and in hot water.

STIBIOTRIMETHYL [$(C_2H_3)_3$ Sb] may be formed in a manner ilar to that directed for stibiotriethyl, which in properties it tly resembles.

6) *Hydrated Oxide of Stibiotetramethylium* [$C_8H_{12}SbO$, $H_3)_4SbO$, HO].—When stibiotrimethyl is brought into ith iodide of methyl the two bodies combine, and a crysde of stibiotetramethylium *is the result*:—

$$\overbrace{(C_2H_3)_3Sb}^{\text{Stibiotrimethyl.}} + \overbrace{C_2H_3I}^{\text{Iodide of methyl.}} = \overbrace{(C_2H_3)_4Sb,I.}^{\text{Iodide of stibiotetramethylium.}}$$

This compound is soluble in boiling water and in alcohol, fro either of which solutions it may be obtained in crystals. Wh treated with oxide of silver, hydrated oxide of stibiotetramethylium i separated, whilst iodide of silver is formed. This oxide is free soluble in water and in alcohol. Its solution is very caustic, a absorbs carbonic acid from the air, presenting most of the us characters of an ammonium base, and precipitating many of th metallic oxides from their salts. Upon evaporating its aque solution *in vacuo*, the oxide may be obtained in crystals, which heated with due care in a tube, may be volatilized without und going decomposition. Its salts are very stable and are rea soluble; they have a bitter taste, but are not poisonous: they p sent great similarity in appearance to those of potash and ammo On the addition of soda or potash to their solutions, the oxide stibio-tetramethylium is liberated.*

§ VI. On the Hydrocarbons derivable from the Alcohols.

(1037) Allusion has already been made to a series of hyd carbons homologous with olefiant gas, which are derivable fr the alcohols, and the process of preparing olefiant gas itself h been described (399). But besides the homologues of olefiant g two additional series of hydrocarbons may be obtained from t alcohols; for the discovery of these compounds we are indebt to the researches of Kolbe and Frankland. One series of the bodies $(C_{2n}H_{2n-1})_2$ corresponds to the radicle of the alcohol, t other $(C_{2n}H_{2n-1}, H)$ to the hydride of that radicle. The table the following page contains the more important members of e of these groups at present known. Another series of the fo $C_{2n}H_{2n-2}$ is represented by acetylene, a gaseous compound recen discovered by Berthelot.

(a) *On the Hydrocarbon Radicles of the Alcohols* $(C_{2n}H_{2n+1})$

(1038) The first substance of this class which was obtaine

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* In addition to the papers already cited on the organo-metallic c pounds, the reader may consult Cahours, *Ann. de Chimie*, III. lviii. 5 B ton, *Phil. Trans.*, 1859, for organo-metallic compounds of tin, mercury, lead; Breed, *Liebig's Annal.* lxxxii. 106, and Dunhaupt, *Ib.* xcii. 371, fo compounds of bismuth.

1. Alcohol Radicles $(C_{2n}H_{2n+1})_2$.					Hydrides of Alcohol Radicles $(C_{2n}H_{2n+1}H)$.					3. Olefiant Gas Series $(C_{2n}H_{2n})''$.				
	Formula.	Boiling point ° F.	Specific Gravity.			Formula.	Boiling point ° F.	Specific Gravity.			Formula.	Boiling point ° F.	Specific Gravity.	
			Liquid.	Vapour.				Liquid.	Vapour.				Liquid.	Vapour.
Methyl .	$(C_2H_3)_2$			1·036	Marsh gas (Hydride of methyl)	C_2H_3,H			0·557	Methylene	C_2H_2?			0·490
Ethyl . .	$(C_4H_5)_2$	—9·4		2·046	Hydride of ethyl .	C_4H_5,H			1·075	Olefiant gas (Ethylene)	C_4H_4			0·978
Trityl . .	$(C_6H_7)_2$									Tritylene (Propylene)	C_6H_6			1·498
Tetryl (Butyl)	$(C_8H_9)_2$	222·8	0·705	4·070	Hydride of tetryl .	C_8H_9,H				Oil gas (Tetrylene) Butylene)	C_8H_8	0		1·852
Amyl . .	$(C_{10}H_{11})_2$	311·0	0·741	4·899	Hydride of amyl .	$C_{10}H_{11},H$	86	0·638	2·5	Amylene .	$C_{10}H_{10}$	102		2·386
Hexyl (Caproyl)	$(C_{12}H_{13})_2$	395·6	0·757	5·983						Hexylene (Caproylene)	$C_{12}H_{12}$	160?		2·875
										Heptylene (Œnanthylene) . .	$C_{14}H_{14}$	210	0·718	3·32
Octyl (Capryl)	$(C_{16}H_{17})_2$									Octylene (Caprylene)	$C_{16}H_{16}$	257	0·723	3·90
										Nonylene (Elaene)	$C_{18}H_{18}$	230?		4·4
										Paramylene	$C_{20}H_{20}$	320		5·0
										Cetylene .	$C_{32}H_{32}$	527		8·0

an isolated form, corresponds in composition to the radicle of tetrylic alcohol, which was procured by Kolbe during the electrolysis of valerate of potash, and was by him termed valyl $(C_8H_9)_2$; other hydrocarbons homologous with tetryl (or, rather, tetrylide of tetryl), have been obtained by the electrolytic decomposition of the salts of the volatile fatty acids (871, 1103); and subsequently a general method of obtaining these bodies was contrived by Frankland, who decomposes the hydriodic ether of the alcohol by means of zinc, at a high temperature in sealed tubes. Greville Williams subsequently succeeded in isolating tetryl $(C_8H_9)_2$, and several other hydrocarbons of this class, from the products of the destructive distillation of Boghead cannel at low temperatures.

The hydrocarbons of this group have not hitherto been made to combine directly with chlorine, bromine, or iodine, so as to reproduce the corresponding hydrochloric, hydrobromic, or hydriodic ether; no action occurs between these bodies and chlorine, or the other halogens, so long as light is excluded, but if light be admitted various substitution compounds are produced. Some chemists, including Hofmann and Gerhardt, when Frankland first announced the isolation of these compounds, considered the non-occurrence of direct combination with chlorine as a strong argument against the admission of the view that they were truly alcohol radicles, and they proposed to view them as homologues of marsh gas: but the subsequent isolation of the true homologues of marsh gas which constitute the hydrides of the alcohol radicles (1041), has neutralized this objection. The bodies which have been termed alcohol radicles, may very consistently be regarded as analogues of hydrogen gas, which many chemists suppose, when in its free state, not to be a simple body, but a compound of hydrogen with itself,—in short, a hydride of hydrogen $\left.\begin{matrix}H\\H\end{matrix}\right\}$, and the so called radicle of alcohol may in like manner be considered as ethylide of ethyl, $\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}$, a view, the correctness of which, the discovery of the double radicles of Wurtz (to which we shall presently refer) may be said to have proved. The alcohol radicles are not absorbed by anhydrous sulphuric acid, or by oil of vitriol, but are completely soluble in alcohol.

These hydrocarbons appear to belong to the hydrogen or metallic type $\left.\begin{matrix}H\\H\end{matrix}\right\}$, and are represented by the formula $\left.\begin{matrix}C_{2n}H_{2n+1}\\C_{2n}H_{2n+1}\end{matrix}\right\}$ a molecule of the compound $(C_{2n}H_{2n+1})_2$ yielding 4 volumes of vapour. They would therefore stand to the third series of hydrocarbons ($C_{2n}H_{2n+2}$), which are to be described shortly (1041), in a relation similar to that of ether to alcohol, thus :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2}^{\text{Ether.}} \qquad ; \qquad \overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}}^{\text{Ethylide of ethyl.}} \qquad ;$$

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}} \qquad ; \qquad \overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}^{\text{Hydride of ethyl.}} \qquad .$$

Wurtz (*Ann. de Chimie,* III. xliv. 275), following up the ideas of Williamson and of Brodie upon the double ethers, has succeeded in obtaining compounds in which the second semi-molecule of the hydrocarbon is displaced by the semi-molecule of the hydrocarbon of a different alcohol, thus forming a series of double radicles corresponding with Williamson's double ethers. If a mixture of the hydriodic ethers of the two alcohols in equivalent proportions be decomposed by means of sodium, the two radicles combine at the moment of their liberation, and form a new double radicle. Thus, in the preparation of ethyl-amyl, the following reaction occurs :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}^{\substack{\text{Iodide of}\\\text{ethyl.}}} + \overbrace{\left.\begin{matrix}C_{10}H_{11}\\I\end{matrix}\right\}}^{\substack{\text{Iodide of}\\\text{amyl.}}} + \left.\begin{matrix}Na\\Na\end{matrix}\right\} = 2\left(\left.\begin{matrix}Na\\I\end{matrix}\right\}\right. + \overbrace{\left.\begin{matrix}C_4H_5\\C_{10}H_{11}\end{matrix}\right\}}^{\text{Ethyl-amyl.}}.$$

The discovery of these compounds confirms in a striking manner the following ingenious explanation by Brodie (*Q. J. Chem. Soc.*, iii. 411), of the mode in which these alcohol radicles are produced:— When zinc is made to decompose anhydrous iodide of ethyl, the first effect does not consist in the liberation of ethyl, but in the formation of a new compound, zinc-ethyl. This stage is rendered more evident by mixing the iodide of ethyl with its own bulk of ether, in which liquid the products of the reaction are soluble. Thus ;—

$$\overbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}^{\text{Iodide of ethyl.}} + \left.\begin{matrix}Zn\\Zn\end{matrix}\right\} = \overbrace{\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}}^{\text{Zinc-ethyl.}} + \left.\begin{matrix}Zn\\I\end{matrix}\right\}.$$

This zinc-ethyl then reacts upon a fresh portion of iodide of ethyl, and thus the ethyl, or rather ethylide of ethyl, is produced by an ordinary double decomposition; the semi-molecule of ethyl from zinc-ethyl, combining at the moment of its liberation with the semi-molecule of ethyl from the iodide of ethyl, as thus represented :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}^{\text{Iodide of ethyl.}}+\overbrace{\left.\begin{matrix}C_4H_5\\Zn\end{matrix}\right\}}^{\text{Zinc-ethyl.}}=\left.\begin{matrix}Zn\\I\end{matrix}\right\}+\overbrace{\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}}^{\text{Ethylide of ethyl.}}$$

If water be present, the result is the formation of a hydrocar of a different kind, which may be regarded as ethyl in which of the semi-molecules of ethyl is displaced by hydrogen.* In case the decomposition would be :—

$$2\,\overbrace{\left.\begin{matrix}C_4H_5\\I\end{matrix}\right\}}^{\text{Iodide of ethyl.}}+2\begin{pmatrix}Zn\\Zn\end{pmatrix}+\left.\begin{matrix}H\\H\end{matrix}\right\}O_2=2\,\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}}^{\text{Hydride of ethyl.}}+2\left.\begin{matrix}Zn\\I\end{matrix}\right\}+\left.\begin{matrix}Zn\\Zn\end{matrix}\right\}O_2.$$

Wurtz's double radicles would therefore be merely compound which the place of the semi-molecule of hydrogen, or of the et was supplied by a different hydrocarbon :—

Hydride of ethyl	C_4H_5,H.
Ethyl (ethylide of ethyl) . . .	C_4H_5,C_4H_5.
Ethyl-amyl (ethylide of amyl) . .	$C_4H_5,C_{10}H_{11}$.

It is interesting to remark, that the boiling point of t double radicles rises gradually as the number of atoms of ca and hydrogen increases in the compound molecule, and that regular progression is observed in the simple alcohol radicles w compared with them, as in the following table; the boiling p and vapour density of the simple alcohol radicles being suc would theoretically be assigned to them upon the view a given; showing that both the simple and the double radicles formed upon a similar molecular plan :—

Double Radicles.	Formulæ. (Each yielding four volumes of vapour.)	Boiling point ° F.	Specific Gravity. Vapour. Expt.	Specific Gravity. Vapour. Theory.	Li
Ethyl (Ethylide of ethyl) . .	$C_8H_{10}=C_4H_5,C_4H_5$	−9·4	2·046	2·004	
Ethyl-tetryl . .	$C_{12}H_{14}=C_4H_5,C_8H_9$	143·6	3·053	2·972	0·
Ethyl-amyl . .	$C_{14}H_{16}=C_4H_5,C_{10}H_{11}$	190·4	3·522	3·455	0·
Methyl-hexyl . .	$C_{14}H_{16}=C_2H_3,C_{12}H_{13}$	179·6?	3·426	3·455	
Tetryl (Tetrylide of tetryl) . .	$C_{16}H_{18}=C_8H_9,C_8H_9$	222·8	4·070	3·939	0·
Tetryl-amyl . .	$C_{18}H_{20}=C_8H_9,C_{10}H_{11}$	269·6	4·465	4·423	0·
Amyl (Amylide of amyl) . .	$C_{20}H_{22}=C_{10}H_{11},C_{10}H_{11}$	311	4·899	4·907	0·
Tetryl-hexyl . .	$C_{20}H_{22}=C_8H_9,C_{12}H_{13}$	311	4·917	4·907	
Hexyl (Hexylide of hexyl) . .	$C_{24}H_{26}=C_{12}H_{13},C_{12}H_{13}$	395?	5·983	5·874	0·

---

* At present no compound of zinc with hydrogen (HZn) correspond zinc-ethyl is known, though there is nothing improbable in the supp that such a body may hereafter be obtained.

It may further be remarked, in illustration of the persistence the original molecular arrangement of the component groups of se compound bodies, that Wurtz finds that amyl preserves rotatory action on a ray of polarized light when it passes these compounds, ethyl-amyl displaying the power of rotat- a polarized ray to the right; whilst amylene, valeric acid, other derivatives of amylic alcohol, in which there is reason to pose that the molecule of amyl is destroyed, exert no rotatory er.

(1039) 1. *Methyl* [$(C_2H_3)_2$: *Sp. gr.* 1·0365] is a gaseous body ich burns with a bluish feebly luminous flame; it is not efied by a cold of 0° F. Methyl is obtained by acting upon ide of methyl with zinc, exactly in the manner directed for preparation of ethyl. When mixed with twice its bulk of orine in the dark, and afterwards brought into diffused daylight, change of volume takes place, but a mixture of 2 volumes hydrochloric acid, and 1 volume of a chlorinated compound, H_3Cl, is formed.

2. *Ethyl* $(C_4H_5)_2$: *Sp. gr. of gas* 2·046.—When a mixture of nulated zinc and iodide of ethyl is sealed up in a strong s tube from which air has been exhausted, and exposed for two s in an oil bath to a temperature of 300°, the iodide of ethyl gradually decomposed; the sides of the tube become coated with hite crystalline substance, and a colourless mobile liquid, equal lk to about half that of the iodide of ethyl employed, is ed. This liquid is a mixture of ethyl, with other hydrocar- s (olefiant gas, and hydride of ethyl, the product of a secondary mposition), the hydrocarbons having been liquefied by the re of their own vapour, whilst the crystals consist of a com- d of zinc-ethyl (C_4H_5,Zn) with iodide of zinc. On breaking the capillary extremity of the tube under water, the whole of liquid portion disappears rapidly and escapes in the gaseous m. By collecting the portions which pass off last, the ethyl, which the least volatile of these gases, is obtained nearly in a state of rity (Frankland, *Q. J. Chem. Soc.* ii. 281). Ethyl may also be ined, mixed with ethylene and hydride of ethyl, when iodide ethyl is exposed over mercury to the sun's rays, iodide of ury being produced.

Ethyl is a colourless gas with a slight ethereal smell; it burns a highly luminous flame. At a temperature of 0° it remains under the ordinary atmospheric pressure, but it becomes fied at 38°, under a pressure of 2½ atmospheres. Frankland tes its boiling point at about —9°, when the barometer stands at 30 inches. Ethyl is insoluble in water, but freely soluble in alcohol, which dissolves about 18 times its bulk of the gas, and gives it off when diluted with water. Chlorine has no action upon ethyl in the dark, but in diffused daylight it immediately combines with it and forms a colourless liquid.

3. *Trityl* $(C_6H_7)_2$.—The properties of this compound have not been minutely examined; but it formed one of the hydrocarbons separated by Williams from the lighter portion of the distillate from Boghead cannel at low temperatures. (*Note* p. 125.)

4. *Tetryl, Butyl,* or *Valyl* $(C_8H_9)_2$: *Sp. gr. of liquid* 0·7057 at 32°; *of vapour* 4·070; *Boiling pt.* 222°·8.—This compound is one of the products of the distillation of coal at low temperatures, and it may likewise be obtained during the electrolysis of the valerate of potash (871). It may also be prepared by the action of sodium upon iodide of tetryl, in a flask connected with a vertical condenser, so arranged that the volatilized products shall return constantly into the flask as fast as they are volatilized and condensed. When the reaction has terminated, the tetryl may be distilled off by a temperature not exceeding 300°.

5. *Amyl* $(C_{10}H_{11})_2$: *Sp. gr. at* 32°, 0·7413; *of vapour* 4·899; *Boiling pt.* 311°.—Frankland obtained this hydrocarbon by heating iodide of amyl with an amalgam of zinc in sealed tubes for some hours to a temperature of from 320° to 360°. It is one of the products of the distillation of coal, and may also be procured by the electrolysis of caproate of potash, or still more easily as advised by Wurtz, by the action of sodium on iodide of amyl. It is a colourless liquid, with a somewhat aromatic odour. It exerts a right-handed rotatory action on a ray of polarized light, the degree of which appears to vary in different specimens, being connected with the power exerted by that of the fousel oil from which the radicle was prepared, some samples of fousel oil having a greater rotatory power than others.

6. *Hexyl, or caproyl* $(C_{12}H_{13})_2$ was obtained by the voltaic decomposition of œnanthylate of potash. It is a liquid of an agreeable aromatic odour: its boiling point is about 395°.

(1040) Double or Mixed Hydrocarbon Radicles.—*Ethyl-tetryl* (C_4H_5,C_8H_9): *Sp. gr. of liquid at* 32°, 0·7011; *of vapour* 3·053.—This compound was obtained by decomposing a mixture of 40 parts of iodide of tetryl, and 34 of iodide of ethyl, with 11 of sodium, in the manner already described for procuring tetryl: by distillation of the product, collecting the portion which passes over between 140° and 155°, and again rectifying it, a mobile liquid is obtained, the boiling point of which when pure is

mary at 143°·6. By a similar method, employing mixtures corresponding hydriodic ethers, Wurtz succeeded in obtain-
ther analogous compounds, which are enumerated in the
page 238.

) *Hydrocarbons homologous with Marsh Gas* ($C_{2n}H_{2n+2}$).

041) When the hydriodic ethers are submitted to the action
c at a high temperature, other hydrocarbons are formed in
on to the radicles already described; the alcohol radicle
undergoing a secondary decomposition into two hydrocar-
which are complementary to each other. Ethyl, for example,
up into olefiant gas and hydride of ethyl; and amyl, in like
r, yields hydride of amyl, and a corresponding hydrocarbon:—

$$\overbrace{C_4H_5, C_4H_5}^{\text{Ethyl.}} \text{ becoming } \overbrace{C_4H_5, H}^{\text{Hydride of ethyl.}} + \overbrace{C_4H_4}^{\text{Olefiant gas.}}; \text{ and}$$

$$\overbrace{C_{10}H_{11}, C_{10}H_{11}}^{\text{Amyl.}} \text{ becoming } \overbrace{C_{10}H_{11}, H}^{\text{Hydride of amyl.}} + \overbrace{C_{10}H_{10}}^{\text{Amylene.}}.$$

ydrocarbons of this class are not absorbed by anhydrous
ric acid or by oil of vitriol, and are not acted upon by
ne or by iodine in the dark, but in diffused daylight chlorine
gives rise to substitution compounds, and in direct sunlight
mposes them rapidly, often with explosion. Perchloride of
ony is without action upon them.

hese hydrocarbons may also be formed by the regulated
of water upon the metallic compounds of zinc with the
radicles. Thus:—

$$(\overbrace{C_2H_3, Zn}^{\text{Zinc methyl.}})_2 + H_2O_2 = 2\,(\overbrace{C_2H_3, H}^{\substack{\text{Marsh gas, or}\\ \text{Hydride of methyl.}}}) + Zn_2O_2$$

$$(\overbrace{C_4H_5, Zn}^{\text{Zinc ethyl.}})_2 + H_2O_2 = 2\,(\overbrace{C_4H_5, H}^{\text{Hydride of ethyl.}}) + Zn_2O_2$$

$$(\overbrace{C_{10}H_{11}, Zn}^{\text{Zinc amyl.}})_2 + H_2O_2 = 2\,(\overbrace{C_{10}H_{11}, H}^{\text{Hydride of amyl.}}) + Zn_2O_2.$$

erthelot procures the homologues of marsh gas by decom-
the bromide of the corresponding hydrocarbon in the
series by heating it in a sealed tube to 480° with water
le of potassium. The bromide of tritylene ($C_6H_6Br_2$)
the hydride of trityl.

of the hydrocarbons of this group, with the exception of
is isomeric with one of the group of alcohol radicles,
t identical with it; for example:—

		C_2H_4	C_2H_3,H*	Marsh gas
Methyl . . .	C_2H_3,C_2H_3*	$=C_4H_6$	$=C_4H_5,H$*	Hydride of ethyl
Methyl-ethyl .	C_2H_3,C_4H_5	$=C_6H_8$	$=C_6H_7,H$*	Hydride of trityl
Ethyl	C_4H_5,C_4H_5*	$=C_8H_{10}$	$=C_8H_9,H$*	Hydride of tetryl
Methyl-tetryl .	C_2H_3,C_8H_9	$=C_{10}H_{12}$	$=C_{10}H_{11},H$*	Hydride of amyl

Those compounds marked with an asterisk have been already prepared, and others might be easily procured, if needed.

(1042) 1. *Hydride of Methyl* (C_2H_3, H); *Sp. gr.* 0·5596.—This compound has already been described under the name of *marsh gas* (401).

In addition to the mode of preparing it by heating the acetates with a hydrate of one of the alkalies or alkaline earths, marsh gas may be procured by the decomposition of zinc-methyl by water. It may also be obtained from chloroform (C_2HCl_3), or bichloride of carbon (C_2Cl_4), by reducing their alcoholic solutions by means of an amalgam of potassium.

2. *Hydride of Ethyl* (C_4H_5, H); *Sp. gr.* 1·075.—This compound is a permanent gas, destitute of smell or taste. It is insoluble in water, but alcohol takes up more than its own bulk of it. The best manner of preparing this gas consists in decomposing a mixture of equal parts of water and iodide of ethyl, by means of zinc, in a sealed tube, at a temperature of about 330°, as already described when speaking of ethyl (1039). After the lapse of a couple of hours, the tube is opened under water, and the gas escapes with great violence. It may also be obtained by decomposing hydrocyanic ether with potassium. The potassium is placed in a flask, fitted with a condenser and a bent tube for carrying off the gas as it is disengaged; the ether is allowed to fall, drop by drop, upon the potassium, whilst the gas which is disengaged is collected over water. Cyanide of potassium and cyanethine (1000) remain in the flask, and hydride of ethyl is obtained in the gaseous state.

3. *Hydride of Trityl* (C_6H_7, H) is gaseous at ordinary temperatures.

4. *Hydride of Tetryl* (C_8H_9, H) is one of the products of the decomposition of tetrylic alcohol when distilled with chloride of zinc. It is liquefiable at a few degrees below 32°.

5. *Hydride of Amyl* ($C_{10}H_{11}$, H): *Sp. gr. of liquid* 0·638; *of vapour* 2·5; *Boiling pt.* 86°.—This body was obtained by Frankland by acting on equal bulks of iodide of amyl and water, by means of zinc in a sealed tube, at a temperature not exceeding 300°. Frankland considers it to be probable that it is identical with *Eupion*, which Reichenbach obtained during the rectification of the products from wood-tar; and he also thinks that it constitutes one of the condensible hydrocarbons of coal gas.

Hydride of amyl is a volatile, mobile, colourless liquid, with odour resembling that of chloroform. It has a smaller density an any other known liquid; it remains unfrozen at —11°. Its pour burns with a brilliant white flame, without smoke.

(*c*) *Hydrocarbons of the form* $C_{2n}H_{2n-2}$.

(1043) The representative of this class of hydrocarbons is tylene, but a second (C_6H_4), *allylene*, has lately been announced.

Acetylene (C_4H_2) *Sp. gr. calcd.* 0·898, *by expt.* 0·92.—If nobrominated ethylene (C_4H_3Br) be subjected to the action of ium-fousel oil at 212°, under pressure, gradual decomposition es place, bromide of sodium, and amylic alcohol are produced; a permanent gas which is rapidly absorbed by an ammoniacal ution of subchloride of copper is obtained:—

$$\overbrace{C_4H_3Br}^{\text{Brom-ethylene.}}+\overbrace{C_{10}H_{11}NaO_2}^{\text{Sodium-fousel oil.}}=\overbrace{C_4H_2}^{\text{Acetylene.}}+NaBr+\overbrace{C_{10}H_{12}O_2}^{\text{Fousel oil.}}.$$

If the flocculent red precipitate which is thus occasioned in solution of copper be washed, and treated with hydrochloric l, it is decomposed, and pure acetylene is obtained (Sawitsch). thelot, who first isolated this gas, obtained it by decomposing fiant gas by heat. It is present in coal gas in small quantity, is one of the products furnished by transmitting the vapour lcohol, of aldehyd, or of ether through red-hot tubes. It may adily freed from the hydrocarbons with which it is contami- by causing the mixed gas to pass through a solution of loride of copper in ammonia, which absorbs acetylene rapidly forms with it a flocculent dark-red insoluble compound, which dry detonates powerfully on the application of heat, or on ing a sudden blow.

Acetylene is a transparent colourless gas, of a peculiar dis- able odour; it is somewhat soluble in water. It burns with bright smoky flame. It has not yet been liquefied by cold or ure. Acetylene combines with nitrate of silver, and with of mercury. It also unites with bromine, forming bibro- of acetylene ($C_4H_2Br_2$), and is the type or representative of class of hydrocarbons of the formula $C_{2n}H_{2n-2}$.

ixed with chlorine, acetylene explodes spontaneously almost tely even in diffused light, a portion of carbon being sepa- hen agitated with sulphuric acid the gas is gradually rming a colligated acid, the *acetyl-sulphuric*, which rystallizable salt with *baryta*; *when* the acid is diluted and distilled it yields a liquid which is metameric with aldehyd, which Berthelot terms *acetylic alcohol* ($C_4H_4O_2$), the nature of which, however, is at present uninvestigated.

Acetylene may be reconverted into olefiant gas by acting upon its compound with subchloride of copper by means of nascent hydrogen; this change is best effected by suspending the compound of acetylene with subchloride of copper in a solution of ammonia, and adding zinc.

(*d*) *Hydrocarbons homologous with Olefiant Gas* ($C_{2n}H_{2n}$).

(1044) The compounds of this series may be obtained by the decomposition of the hydrochloric ether of the particular alcohol by exposing it to an elevated temperature; under these circumstances the ether is resolved into hydrochloric acid, and the hydrocarbon of the alcohol; thus, C_4H_5Cl becomes $C_4H_4 + HCl$. But they are generally formed by the action of sulphuric acid or of chloride of zinc upon their corresponding alcohols, from which their formulæ differ by containing the elements of two atoms less of water; for instance,—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}} - H_2O_2 = \overbrace{C_4H_4}^{\text{Olefiant gas.}}; \text{ and}$$

$$\overbrace{C_{10}H_{12}O_2}^{\text{Fousel oil.}} - H_2O_2 = \overbrace{C_{10}H_{10}}^{\text{Amylene.}}.$$

The formation of these compounds, however, does not appear to consist simply in the abstraction of water from the alcohol; for, in some cases, the substance which is obtained has a vapour-density double of that which the corresponding hydrocarbon should possess: when, for instance, fousel oil is distilled with sulphuric acid, the hydrocarbon which is liberated is not amylene ($C_{10}H_{10}$); for it has undergone condensation, and has been converted into the polymeric paramylene ($C_{20}H_{20}$), the vapour of which has a density exactly double of that of the true amylene obtained by distilling fousel oil with chloride of zinc.

These hydrocarbons were regarded by Liebig as hydrides of the hydrocarbon radicles of the fatty acids; thus he represented olefiant gas as consisting of (C_4H_3, H), or as the hydride of the hydrocarbon radicle of acetic acid.

The researches of Wurtz and of Hofmann have, however, shown that these bodies are truly diatomic in their nature: olefiant gas (C_4H_4) being equivalent, in combination, to 2 atoms of hydrogen, as will be seen when glycol (1045 *et seq.*) and its derivatives are described.

The hydrocarbons of this class combine readily with sulphuric anhydride, and with perchloride of antimony: ethylene and tritylene are also slowly absorbed by oil of vitriol when briskly agitated with it, and the solution when diluted with water and distilled, yields the corresponding alcohol. The hydrocarbons of this class also combine directly with hydrochloric and with hydrobromic acid, and when heated with them to 212° in the gaseous form for many hours, they become converted into the corresponding hydrochloric or hydrobromic ether. Each molecule of these hydrocarbons also combines with two atoms of chlorine, bromine, and iodine, forming compounds which correspond with Dutch liquid in composition, and from which a similar series of substitution products may be obtained; for example, we may form—

Ethylic Dutch liquid $(C_4H_4)''Cl_2$, or C_4H_3Cl, HCl.
Tritylic do do. $(C_6H_6)''Cl_2$, or C_6H_5Cl, HCl.
Amylic do do. $(C_{10}H_{10})''Cl_2$, or $C_{10}H_{11}Cl$, HCl.

The following are the more important of these hydrocarbons:—

1. *Methylene* (C_2H_2).—Dumas and Péligot believed that they obtained this gaseous body by transmitting the gaseous chloride of methyl through a red-hot porcelain tube; C_2H_3Cl becoming $C_2H_2 + HCl$; but there is some doubt whether the gas which they analysed was anything more than a mixture.

2. *Ethylene, Olefiant Gas,* or *Elayl* (C_4H_4) has already been described (399).—It is produced, abundantly mixed with other hydrocarbons, during the dry distillation of pit coal, and of many fatty and resinous bodies. It is also present in small quantity, amongst other bodies, in the product of the dry distillation of formiate of baryta. Olefiant gas is the principal luminous constituent of coal gas. When required in a state of purity it is always obtained by decomposing alcohol by means of sulphuric acid in excess.

Berthelot (*Comptes Rendus,* July 28th, 1856) has shown that olefiant gas and marsh gas, in small quantity, diluted largely with free hydrogen, may be obtained by passing a current of sulphuretted hydrogen mixed with the vapour of bisulphide of carbon over finely divided copper heated to dull redness; a process which possesses some interest from the circumstance that it indicates a method, though an imperfect one, for procuring from compounds of inorganic origin, hydrocarbons, which previously had been obtained only by the decomposition of organic products.

3. *Tritylene, Propylene* (C_6H_6), *Sp. gr.* 1·498.—Reynolds obtained this gas mixed with marsh gas and some other compounds, by decomposing the vapours of fousel oil by transmission through a porcelain tube heated to redness; but it is best procured by the action of biniodide of phosphorus (PI_2) upon glycerin. Pure tritylene is readily obtained for laboratory use by distilling 1 part of iodide of allyl (1282) with 5 parts of mercury and 2 parts of concentrated hydrochloric acid. An ounce of iodide of allyl thus yields more than 150 cubic inches of the gas; $C_6H_5I + HCl + 2\,Hg_2 = C_6H_6 + Hg_2I + Hg_2Cl$. Tritylene remains gaseous at—40°, but it may be liquefied under pressure. Its odour resembles that of olefiant gas. It is dissolved to some extent by essence of turpentine, ether, chloroform, and benzol, each of which dissolves from 13 to 18 times its volume of this gas.

Oil of vitriol readily absorbs about 200 times its volume of the gas, converting it into sulphotritylic acid. Hydrochloric acid also absorbs it, and forms trityl-hydrochloric ether or iodide of trityl, C_6H_7Cl. The action of iodine and of bromine upon tritylene yields compounds of considerable interest in connexion with the allylic series.

4. *Tetrylene, Butylene,* or *Oil Gas* (C_8H_8), has been already described (405).—This gas was ascertained by Faraday to be one of the products furnished by the destructive distillation of oil; and it appears also to be contained amongst the products of the distillation of caoutchouc. It was afterwards obtained by Kolbe during the voltaic decomposition of valerate of potash; and by Wurtz as one of the compounds produced by the action of chloride of zinc upon tetrylic alcohol.

5. *Amylene* ($C_{10}H_{10}$; *Boiling pt.* 102°) may be procured by decomposing chloride of amyl by fused hydrate of potash, or by distilling a concentrated solution of chloride of zinc with fousel oil; or by acting upon iodide of amyl in a sealed tube with an amalgam of zinc: in the latter case it is mixed with hydride of amyl. Amylene is a colourless, very mobile liquid, with the odour of decaying cabbage. An attempt was made to substitute it for chloroform as an anæsthetic in surgical operations; but its use has been abandoned, as in some cases its employment has occasioned fatal results.

6. *Hexylene* or *Caproylene* ($C_{12}H_{12}$); *Boiling pt.* 160° (Williams).—This compound is a colourless liquid lighter than water, of a nauseous, penetrating, alliaceous odour. It is scarcely soluble in water, but freely so in alcohol and ether. It appears to act injuriously when respired. It is procured during the destructive

istillation of several fatty acids (Fremy), and is one of the products obtained by Williams from the distillation of the Boghead annel.

7. *Heptylene* or *Œnanthylene* ($C_{14}H_{14}$); *Sp. gr. of liquid* 0·718; *of vapour* 3·32; *Boiling pt.* 210°.—This body was also found by Williams in the Boghead distillate; and was likewise obtained by Bouis from the distillation of œnanthol (1083) with anhydrous phosphoric acid.

8. *Octylene* or *Caprylene* ($C_{16}H_{16}$; *Boiling pt.* 257°), was obtained as a colourless liquid, insoluble in water, by distilling the castor oil (octylic) alcohol with sulphuric acid, or chloride of zinc. The action of potassium or of mercury on chloride or iodide of octyl gives rise to the same compound:—

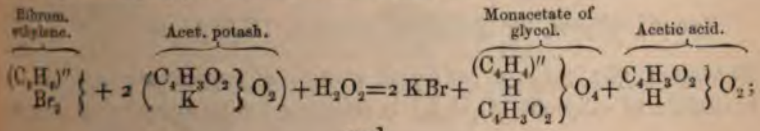
$$2\,C_{16}H_{17}I + 2\,Hg_2 = 2\,C_{16}H_{16} + 2\,Hg_2I + H_2.$$

9. *Nonylene*, or *Elaene* ($C_{18}H_{18}$) was obtained mixed with hexylene, by Fremy, during the distillation of several fatty acids.

10. *Paramylene* ($C_{20}H_{20}$) is procured by the distillation of fousel oil with anhydrous phosphoric acid in excess. Its boiling point is as high as 320°, that of amylene being only 102°. Fousel oil, it will be seen, gives rise to at least three isomeric hydrocarbons of this series, viz., to tritylene, amylene, and paramylene, and even as Bulard believes, to one of still greater density.

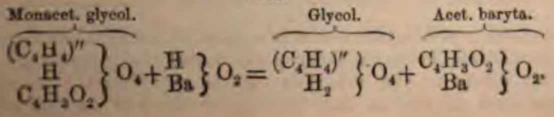
DIATOMIC ALCOHOLS, OR GLYCOLS.

(1045) THE GLYCOLS, as it has already been stated, are a purely artificial class of compounds, the existence of which, as an intermediate series between the monobasic alcohols and the glycerins, was inferred by Wurtz. They are formed from ethylene and its homologous diatomic hydrocarbons. They are procured by preparing the bibromide or the biniodide of the hydrocarbon, and decomposing it with acetate of potash or acetate of silver, and obtaining the monacetate or binacetate of the glycol, (1046) and on distilling these compounds with hydrate of baryta, or hydrate of potash, the corresponding glycol is liberated; for example:—



$$\overbrace{\left.\begin{matrix}(C_4H_4)''\\Br_2\end{matrix}\right\}}^{\text{Bibrom. ethylene.}} + 2\left(\overbrace{\left.\begin{matrix}C_4H_3O_2\\K\end{matrix}\right\}O_2}^{\text{Acet. potash.}}\right) + H_2O_2 = 2\,KBr + \overbrace{\left.\begin{matrix}(C_4H_4)''\\H\\C_4H_3O_2\end{matrix}\right\}O_4}^{\text{Monacetate of glycol.}} + \overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2}^{\text{Acetic acid.}};$$

and



$$\overbrace{\left.\begin{matrix}(C_4H_4)''\\H\\C_4H_2O_2\end{matrix}\right\}O_4}^{\text{Monacet. glycol.}} + \left.\begin{matrix}H\\Ba\end{matrix}\right\}O_2 = \overbrace{\left.\begin{matrix}(C_4H_4)''\\H_2\end{matrix}\right\}O_4}^{\text{Glycol.}} + \overbrace{\left.\begin{matrix}C_4H_3O_2\\Ba\end{matrix}\right\}O_2}^{\text{Acet. baryta.}}.$$

By analogous reactions the following compounds have been prepared :—

Compound.	Formula.	Boiling point. °F.	Specific Gravity.	
			Liquid.	Vapour.
Glycol	$\left.\begin{matrix}(C_4H_4)''\\H_2\end{matrix}\right\}O_4$	387	1·125	2·164
Trityl-glycol (Propyl-glycol) . .	$\left.\begin{matrix}(C_6H_6)''\\H_2\end{matrix}\right\}O_4$	371	1·051	2·596
Tetryl-glycol (Butyl-glycol) . .	$\left.\begin{matrix}(C_8H_8)''\\H_2\end{matrix}\right\}O_4$	362	1·048	3·188
Amyl-glycol	$\left.\begin{matrix}(C_{10}H_{10})''\\H_2\end{matrix}\right\}O_4$	351	0·987	

Each of these glycols corresponds to a monatomic alcohol which contains 2 atoms less of oxygen :—

$$\overbrace{C_4H_6O_2}^{\text{Alcohol.}}\ ;\ \overbrace{C_6H_8O_2}^{\text{Trityl-alcohol.}}\ ;\ \overbrace{C_8H_{10}O_2}^{\text{Tetryl-alcohol.}}\ ;\ \overbrace{C_{10}H_{12}O_2}^{\text{Amyl-alcohol.}}.$$

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}}\ ;\ \overbrace{C_6H_8O_4}^{\text{Trityl-glycol.}}\ ;\ \overbrace{C_8H_{10}O_4}^{\text{Tetryl-glycol.}}\ ;\ \overbrace{C_{10}H_{12}O_4}^{\text{Amyl-glycol.}}.$$

The glycols when exposed to the action of air or oxygen under the influence of platinum black, or when heated with hydrate of potash speedily become oxidized, and furnish acids which belong to the lactic or the oxalic acid series :—

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}}+O_4 = \overbrace{C_4H_4O_6}^{\text{Glycolic acid.}}+\ H_2O_2\text{; and}$$

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}}+O_8 = \overbrace{C_4H_2O_8}^{\text{Oxalic acid.}}+2\ H_2O_2.\text{*}$$

It will be unnecessary to enter minutely into a description of the glycols, as the general properties of these compounds will be sufficiently understood from the following account of ethylic glycol; for further details the reader is referred to Wurtz's paper on the subject. (*Ann. de Chimie*, III., lv., 400.)

(1046) *Glycol,* or *Ethylene Alcohol,* $[C_4H_6O_4=\left.\begin{matrix}(C_4H_4)''\\H_2\end{matrix}\right\}O_4]$; *Boiling pt.* 387°; *Sp. gr. of liquid* 1·125; *of vapour* 2·164.—When biniodide of ethylene ($C_4H_4I_2$) is triturated with anhydrous acetate

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* It is indeed possible that there is a class of compounds represented by glyoxal, intermediate between these glycols and the glycolic or lactic acid series, corresponding to the aldehyds of the monobasic alcohols (Debus); and the researches of Debus have further rendered it not unlikely that be-

r, in the proportion of 10 parts or one atom of the former
arts or 2 atoms of the latter, and the mixture is introduced
flask, a brisk reaction speedily begins to take place; the
ture rises, and the mass becomes yellow, owing to the
on of iodide of silver; while carbonic acid and olefiant gas,
lt of a secondary decomposition, are evolved in abundance.
duct of this reaction is then to be submitted to distillation,
portions which come over between 320° and 400°, are to be
separately, and rectified from litharge. By repeating the
n and collecting the product in separate portions, a liquid
th obtained which boils at 365°, and may be distilled
ndergoing decomposition. This liquid is the *binacetate*
nd if the secondary products of the reaction be neg-
ormation may be thus represented :—

$$+2\,\overbrace{(AgO,C_4H_3O_3)}^{\text{Acetate of silver.}} = 2\,AgI + \overbrace{C_4H_4O_2,\ 2\,C_4H_3O_3}^{\text{Binacetate of glycol.}}.$$

te of glycol is a colourless neutral liquid, which emits
odour when heated. It is heavier than water, in
it slightly soluble: alcohol dissolves it freely.

e of glycol appears to be formed when biniodide of
cted upon by anhydrous benzoate of silver; other
likewise attack the biniodide of ethylene with facility,
s compound glycolic ethers may be obtained without

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nd the oxalic series of acids is a third intermediate group of
ntative of which is the glyoxalic (1002), so that the different
lation of glycol would be the following:—

$$2\,\overbrace{C_4H_6O_4}^{\text{Glycol.}}+2\,O_4=2\,\overbrace{C_4H_4O_6}^{\text{Glycolic acid.}}+2\,H_2O_2.$$

$$2\,\overbrace{C_4H_6O_4}+2\,O_4=2\,\overbrace{C_4H_2O_4}^{\text{Glyoxal.}}+4\,H_2O_2.$$

$$2\,\overbrace{C_4H_6O_4}+3\,O_4=2\,\overbrace{C_4H_2O_6}^{\text{Glyoxalic acid.}}+4\,H_2O_2.$$

$$2\,\overbrace{C_4H_6O_4}+4\,O_4=2\,\overbrace{C_4H_2O_8}^{\text{Oxalic acid.}}+4\,H_2O_2.$$

f these bodies may further be thus represented:—

$C_4H_6O_4$ Glycol.
$C_4H_4O_4$ Aldehyd (as yet unknown).
$C_4H_4O_6$ Glycolic acid.
$C_4H_4O_8$ Acid (as yet unknown).
$C_4H_2O_4$ Second aldehyd (glyoxal).
$C_4H_2O_6$ Glyoxalic acid.
$C_4H_2O_8$ Oxalic acid.

When binacetate of glycol is digested upon powdered hydrate of baryta, or hydrate of potash, an energetic action speedily commences; but the mixture must be maintained at a temperature of about 360° for a few hours, in order that the decomposition may be complete: if it be then submitted to distillation, glycol passes over, and may be purified by fractionated distillation.

Glycol is a colourless, slightly viscous liquid, with a sweet taste. It does not solidify even in the cold produced by a bath of carbonic acid and ether. It may be distilled unaltered, and yields an inflammable vapour. It is soluble in water, and in alcohol, in all proportions. Ether does not dissolve it in any considerable quantity. Glycol is immediately attacked by sodium; hydrogen is disengaged, and a white saline mass is formed ($C_4H_5NaO_4$), *mono-sodium glycol*, which, when heated with more sodium in an oil bath to 374°, fuses, and is gradually converted into a white deliquescent mass, *di-sodium glycol* $(C_4H_4)''Na_2O_4$, or glycol which contains 2 atoms of sodium in the place of 2 of hydrogen. If glycol be heated with hydrate of potash it experiences oxidation, and pure hydrogen is evolved, whilst oxalate of potash is the chief product in the residue:—

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}} + 2\,(KO,HO) = \overbrace{2\,KO,C_4O_6}^{\text{Oxal. potash.}} + 4\,H_2.$$

Glycol is also oxidized with great energy by nitric acid, oxalic acid being formed in abundance; if the acid be allowed to mix very gradually by diffusion into glycol diluted with twice its bulk of water, the product of the oxidation is chiefly glycolic acid. If the same experiment be made with tritylic glycol, lactic acid is the result of the oxidation:—

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}} + O_4 = \overbrace{HO,C_4H_3O_5}^{\text{Glycolic acid.}} + H_2O_2$$

$$\overbrace{C_6H_8O_4}^{\text{Trityl-glycol.}} + O_4 = \overbrace{HO,C_6H_5O_5}^{\text{Lactic acid.}} + H_2O_2.$$

(1047) *Ethers of Glycol.*—When glycol is saturated with hydrochloric acid, and heated in a sealed tube to 212° for 24 hours, combination between the two takes place, whilst water is separated:—

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}} + HCl = \overbrace{C_4H_5ClO_2}^{\text{Chlorhydrin of glycol.}} + H_2O_2.$$

This body is a neutral, colourless liquid, freely soluble in water, boiling at 262°. A solution of potash instantly decomposes it, furnishing a volatile liquid, *binoxide of ethylene* $(C_4H_4)''O_2$; *Sp. gr.*

pour 1·422; *Boiling pt.* 56°. This body is metameric with hyd, but has a lower boiling point, and it does not form any alline compound with ammonia. It is polymeric with lic ether $(C_4H_4)_2''O_4$, a substance which, however, Wurtz een unable to obtain.

n attempting to deprive glycol of water by treatment with ide of zinc, true aldehyd was obtained, mixed with some of its erides:—

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}} - H_2O_2 = \overbrace{C_4H_4O_2}^{\text{Aldehyd.}}.$$

lycol, however, forms compound ethers, in which 1 atom or 2 of acid may be present, according to the proportion of water ated: the first is exemplified in the monacetate of glycol:—

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}} + \overbrace{C_4H_4O_4}^{\text{Acetic acid.}} - H_2O_2 = \overbrace{C_8H_8O_6}^{\text{Monacet. glycol.}};$$

cond case is exemplified in the binacetate of glycol:—

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}} + 2\,\overbrace{C_4H_4O_4}^{\text{Acetic acid.}} - 2\,H_2O_2 = \overbrace{C_{12}H_{10}O_8}^{\text{Binacet. glycol.}}.$$

some cases two different acids are united with the molecule col, as in the acetobutyrate:—

$$\overbrace{C_4H_6O_4}^{\text{Glycol.}} + \overbrace{C_4H_4O_4}^{\text{Acetic acid.}} + \overbrace{C_8H_8O_4}^{\text{Butyric acid.}} - 2\,H_2O_2 = \overbrace{C_{16}H_{14}O_8}^{\text{Acetobutyrate glycol.}}.$$

e bichloride of ethylene, or Dutch liquid, is the true bihyric ether of glycol, and the bibromide of ethylene is bihydroether of glycol.*

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* urtz finds that if oxide of ethylene $(C_4H_4O_2)$ be sealed up in a tube ycol, and heated with it for some hours, a series of compounds are pron which he assigns the following composition, starting with glycol:—

$$\text{Glycol, or ethylene alcohol} \left\{\begin{matrix}(C_4H_4)''\\ H_2\end{matrix}\right\} O_4 = C_4H_6O_4$$

$$\text{Diethylene alcohol}\quad .\ .\quad \left\{\begin{matrix}(C_4H_4)_2''\\ H_2\end{matrix}\right\} O_6 = C_8H_{10}O_6$$

$$\text{Triethylene alcohol}\quad .\ .\quad \left\{\begin{matrix}(C_4H_4)_3''\\ H_2\end{matrix}\right\} O_8 = C_{12}H_{14}O_8.$$

e bodies all resemble alcohols in their properties, and are termed *lene alcohols* by Wurtz, glycol being formed on the diatomic type, e alcohol on the triatomic type, and triethylene alcohol on the c type.

ppears to be not improbable that there are diatomic alcohols in the e groups (972) to which the benzoic and salicylic series belong; for t has been suggested that saligenin (1271) may be the dibasic ich by its oxidation would furnish salicylic acid:—

$$\overbrace{\left.\begin{matrix}C_{14}H_6\\ H_2\end{matrix}\right\} O_4}^{\text{Saligenin.}} + O_4 - H_2O_2 = \overbrace{\left.\begin{matrix}C_{14}H_4O_2\\ H_2\end{matrix}\right\} O_4}^{\text{Salicylic acid.}}$$

t awaits further elucidation from experiment.

[illegible] represents the composition and so
[illegible] more important compounds of

Glycol and its Ethers.

	Formula.	Boiling Point ° F.	Sp Liq
[illegible]	$\left.\begin{matrix}(C_4H_4)''\\H_2\end{matrix}\right\}O_4$	387	1·1
[illegible]	$(C_4H_4)''\ O_2$	56	
[illegible]	$\left.\begin{matrix}(C_4H_4)''\\H\\C_4H_5\end{matrix}\right\}O_4$	about 275	
[illegible]	$\left.\begin{matrix}(C_4H_4)''\\(C_4H_5)_2\end{matrix}\right\}O_4$	254	0·7
[illegible]	$\left.\begin{matrix}(C_4H_4)''\\H\\C_4H_3O_2\end{matrix}\right\}O_4$	360	
[illegible]	$\left.\begin{matrix}(C_4H_4)''\\(C_4H_3O_2)_2\end{matrix}\right\}O_4$	368	1·1
[illegible]	$\left.\begin{matrix}(C_4H_4)''\\(C_8H_7O_2)_2\end{matrix}\right\}O_4$	above 662	
[illegible] glycol . . .	$\left.\begin{matrix}(C_4H_4)''\\C_4H_3O_2\\C_8H_7O_2\end{matrix}\right\}O_4$	406 to 419	
[illegible] of glycol . .	$\left.\begin{matrix}(C_4H_4)''\\C_4H_3O_2\\Cl\end{matrix}\right\}O_2$	293	1·1
[illegible] glycol	$\left.\begin{matrix}(C_4H_4)''\\HCl\end{matrix}\right\}O_2$	262	
[illegible]	$\left.\begin{matrix}(C_4H_4)''\\Cl_2\end{matrix}\right\}$	184	1·2
[illegible] glycol [illegible] ethylene) . .	$\left.\begin{matrix}(C_4H_4)''\\Br_2\end{matrix}\right\}$	265	2·1

CHAPTER IV.

[illegible] OILS.—TRIATOMIC ALCOHOLS, AND T
COMPOUNDS.

§ I. Natural Fats and Oils.

[illegible] proceeding to the examination of th [illegible] glycerin, it will be convenient to [illegible] of its most abundant natural compoun [illegible] constitute an important and well define [illegible] compounds, which are obtained abunda [illegible] the vegetable kingdom. In their relations they present a close analogy with the compound ethers. The predominating elements in their composition are carbon and hydrogen, and as a general rule, the greater the proportion of carbon and the less that of oxygen which they contain, the higher is their melting point. The vegetable fats and oils occur in various parts of the plant, but they are most abundant in the seed. The seeds of the *cruciferæ* are particularly remarkable for the large quantity of oil which they furnish; rapeseed contains from 35 to 40 per cent. of oil, and linseed furnishes more than a fifth of its weight. The fleshy fruit of the olive also yields oil in great abundance, and the same is the case with the *Elais guineensis* or palm oil fruit. In animals, fat is particularly liable to accumulate immediately beneath the cuticle, also in the omentum and around the kidneys. The fatty bodies obtained from warm-blooded animals are generally solid at ordinary temperatures; whilst those from fish and from cold-blooded animals are liquid. In all cases, both in the animal and in the plant, a certain quantity of some albuminoid substance occurs associated with the oily body, and this substance exerts an important chemical influence upon the fat when kept. In the extraction of the oil, simple pressure is generally sufficient to separate it from the cells of the tissue in which it is contained. If it be solid at ordinary temperatures, it may often be procured by boiling the tissue with water; it then rises to the surface and forms a layer which solidifies on cooling.

The fats and oils are lighter than water, having a specific gravity varying from about 0·91 to 0·94; they have different degrees of solidity, and do not consist of any single proximate principle in a state of purity, but are for the most part mixtures, in varying proportions, of at least three different closely allied bodies; two of which, viz., *stearin* (from *στέαρ*, suet) and *margarin* (from *μάργαρον*, a pearl, owing to its pearly lustre), are solid at ordinary temperatures; whilst the third, *olein*, is liquid. The larger the proportion of olein which is present, the softer is the fat, and the lower is its fusing point.

All fats are soluble in ether, and to a certain extent also in alcohol. Oil of turpentine and benzol likewise dissolve them with facility, and the different fats and oils may be mixed with each other in all proportions. They possess the property of rendering paper semitransparent, producing what is well known as a greasy stain. The fats and oils may be heated to nearly 500° without undergoing any important change, but they cannot be distilled without experiencing decomposition. Hence the term, *fixed oils*, is applied to these bodies in contradistinction to that of *volatile oils*, which is given to the fragrant essences obtained from the vegetable kingdom, which may be distilled without alteration. At about 500° the fats and oils begin to give off acrid and offensive vapours, and at a little above 600°, they are rapidly decomposed with evolution of gaseous hydrocarbons, the escape of which gives to the oil the appearance of ebullition; as the result of the distillation, a mixture of solid and liquid hydrocarbons, of water and of various fatty acids, accompanied by a peculiarly irritating substance termed acrolein (1071), are formed and may be condensed in the receiver.

(1049) *General Nature of the Neutral Fats.*—The fatty bodies when heated with the hydrated alkalies, experience a peculiar change, long known under the title of *saponification*, or conversion into soap (1063), during which process all fats yield up a viscid liquid, which, owing to its sweet taste, has been termed *glycerin* (from γλυκὺς, sweet). The nature of this change may be ascertained by dissolving the soap in water, and then adding some acid, such as the tartaric or the hydrochloric, which combines with the alkali and forms a soluble compound with it. Unctuous flocculi are thus separated, and on the application of heat they melt, and form an oily layer on the surface of the fluid. This substance when cold is found to possess properties very different from those of the original fat. It is crystalline, freely soluble in alcohol, and the spirituous solution reddens litmus paper strongly. It possesses distinctly acid characters, and it is soluble at once, and without the appearance of milkiness, in hot alkaline liquids.

This unctuous matter varies in consistence and quality with the nature of the fat from which it is procured, and is for the most part a mixture of three acids (derived from the three bodies already mentioned as forming the greater number of the fats), and termed respectively, *oleic*, *stearic*, and *margaric* acids. It is found that the united weight of the glycerin and of these fatty acids, always exceeds by 3 or 4 per cent. that of the fat originally employed. In fact, the olein, stearin, and margarin are each compounds of their respective fatty acid, with the basis of glycerin, which has been displaced by the alkali in the act of forming soap; the alkali in displacing the base of the glycerin, gives up a portion of water to it, and hence increases its weight; while the fatty acid, on being separated from the soap, also in like manner combines with a portion of water. Simple mixture of the glycerin and of the fatty acid together, therefore, does not again produce the oil or fat from which they were obtained.

The masterly analytical researches of Chevreul upon the fats, have recently received complete explanation in the parallel remarkable synthetic experiments of Berthelot, which have shown that the ordinary varieties of natural fats and oils, are the tribasic ethers of the triatomic alcohol glycerin. We have already seen that compound ethers of the monobasic alcohols by the action of water become converted into the hydrated acid and alcohol; in a similar manner the fats, by saponification, or by the action of water at an elevated temperature, are converted into the hydrated fatty acid, and glycerin. Oxalic ether, for instance, undergoes the following decomposition:—

$$2\,\overbrace{C_4H_5O,C_4O_6}^{\text{Oxalic ether.}} + 2\,H_2O_2 = 2\,\overbrace{(C_4H_5O,HO)}^{\text{Alcohol.}} + 2\,\overbrace{HO,C_4O_6}^{\text{Oxalic acid.}};$$

and the formation of stearic acid and glycerin from stearin, may be represented by an analogous equation; thus:—

$$\overbrace{C_6H_5O_3.3\,C_{36}H_{35}O_3}^{\text{Stearin.}} + 3\,H_2O_2 = \overbrace{C_6H_8O_6}^{\text{Glycerin.}} + \overbrace{3\,(HO,C_{36}H_{35}O_3)}^{\text{Stearic acid.}}.$$

When the oils are mixed with an aqueous solution of the alkalies, saponification takes place slowly, but if the oil be dissolved in alcohol, and then mixed with an alcoholic solution of the caustic alkali, both at a boiling temperature, the saponification is instantaneous and complete.

The saponification of the fats and oils may be effected by heating them with the anhydrous bases, such as caustic lime and oxide of lead: but a large proportion of the glycerin is always destroyed in the operation, for want of water with which it can combine at the moment of its liberation from the fat; and unless the heat be carefully regulated, the fatty acid itself is liable to become decomposed.

When the oily seeds, such as almonds, walnuts, or poppy seeds, are crushed or pulverized, so as to break up the cellular tissue, and bring their several components into mixture with each other, the neutral fatty bodies which the seeds naturally contain are gradually converted into fatty acids, and glycerin is liberated. This change has been shown by Pelouze to depend upon the action of an albuminous ferment contained in the pulp, and to be independent of any absorption of oxygen.

The fats are more fusible than the acids which they furnish on saponification, but, when exposed to a low temperature, they become much harder than the fatty acids. Generally they are destitute of odour and taste; the peculiar scent emitted by some of them depending upon the presence of a small proportion of some glycerin compound of one *of the volatile oily acids,* such as the butyric, valeric, or capric. It is worthy of remark, that although themselves are but sparingly soluble in alcohol, their solu greatly increased by the presence of a free fatty acid. A appears to combine with many of the oils, but it conver into amides, and not into true soaps (Rowney). The com of ammonia with almond oil and with castor oil are crysta

(1050) *Rancidity of Oils.*—Fats and oils are subject to liar change in their properties, popularly distinguished by t 'rancidity.' This change is attended with a slight absor oxygen, and it appears to be due to the decomposition of mucilaginous and albuminous matters contained in the oil during their decay react on the fat, setting free the fatt and decomposing the glycerin. Perfectly pure fats and oil become rancid; and rancidity may be completely removed b ing or washing them first with boiling water, and subse with a cold weak alkaline ley. When the vegetable oils ployed for purposes of illumination, it is necessary to puri from these mucilaginous matters, which otherwise become and encrust the wick, and thus prevent the oil from burning To effect this purification, the oil may be mixed with one of its weight of oil of vitriol, which is to be added in sm tions at a time, keeping the mixture in continual agitation flocculi are thus formed, which subside when the mixture is rest. The supernatant oil is then to be drawn off, and th ing acid is to be removed by agitating it with one-fourth its of water, mingled with a small proportion of lime. Lastly is rendered fit for use by filtration through charcoal.

(1051) *Drying and Non-drying Oils.*—Oils may be arranged under two distinct classes, according as they posse not possess the property of absorbing oxygen, by which t gradually converted into a solid mass; those which becom in this manner, are termed *drying oils*. Some oils, such as oil, in undergoing this change do not evolve any gas; but the solidification of most others, an evolution of carbon attended sometimes with an escape of hydrogen, takes place

The non-drying oils do not absorb oxygen, but are co into elaidin by means of subnitrate of mercury or by per nitrogen, a reaction of which those of the first variety susceptible. The solidification of olive oil is effected by a q of peroxide of nitrogen, not exceeding $\frac{1}{100}$th of the weight oil (1127).

The principal drying oils are those of linseed, walnut, poppy, cod liver, and sperm oil. The absorption of oxy

of these oils, and consequent elevation of temperature, is,
favourable circumstances, so rapid as to be attended with
sufficient to cause the mass to take fire; and several serious
grations have been traced to the spontaneous ignition of
on, wool, or tow, soaked in linseed oil, which had been thrown
in refuse heaps after it had been used in cleaning machinery.
ccative or drying property of these oils may be much in-
d by heating them with about one-twentieth of their weight
tharge, which becomes completely dissolved by the oil. Oxide
nganese may be used for the production of a similar effect:
ed oil which has been thus treated, is technically known as
d oil. Chevreul, however, states that it is unnecessary to heat
oil for so long a time, or to so high a temperature as is com-
ly practised; linseed oil heated to 140° in contact with one-
h of its weight of oxide of manganese, having acquired powerful
tive properties. According to Liebig, the increased rapidity
which oil thus treated becomes hard on exposure to the air,
to the mechanical removal of the impurities of the oil by the
of lead, which allows the oxygen to come more freely into
ct with each particle of the oil.

The drying oils are not solidified by contact with peroxide of
gen, or with subnitrate of mercury, and a fraudulent mixture
n with olive or almond oil may thus be detected. The oleic
which they furnish on saponification, differs from ordinary
acid, and absorbs oxygen much more rapidly than the latter;
in consequence of this oxidation it speedily becomes converted
a transparent solid varnish. For a careful investigation of
changes which occur during the drying of oils, the reader is
red to a paper by Chevreul (*Ann. de Chimie*, III. xlvii. 209).
most important of the oils which do not become dry by ex-
re to the air are olive oil, almond oil, rape oil, and colza oil,
des many animal oils.

Composition and Properties of the principal Oils and Fats.

(1052) 1. *Olive oil* (*sp. gr.* 0·918) is prepared in great abundance
he southern countries of Europe; it furnishes the principal
material employed in making Marseilles and Castile soap.
ripe olives are first subjected to pressure without the appli-
n of heat, and in this manner the finest oil, or *virgin oil*, is
ed; the residue is afterwards heated with water, and a large
y of an inferior mucilaginous oil rises to the surface; it is this
is chiefly employed in soap-making. The oil is always of

much finer quality if extracted immediately after the fru been crushed, as otherwise it experiences a kind of ferment which injures the flavour of the product. The solid ingredi olive oil is almost exclusively margarin. Olive oil soon be rancid when kept; it becomes partially solid at a few de below 32°.

2. *Almond oil* (*sp. gr.* 0·918 at 60°) is much less exten employed than olive oil; it is extracted from the kernel *Amygdalus communis*, by a process similar to that adopted for oil. It solidifies at about —13°.

3. *Colza oil* (*sp. gr.* 0·913), which is largely used for il nating purposes, is obtained from the seeds of the *Brassica ol* It is of a yellow colour, and is nearly free from odour. temperature of 22° F. it becomes nearly solid. Colza o sparingly soluble in cold alcohol, but is readily dissolved by ing alcohol.

4. *Linseed oil* (*sp. gr.* 0·939 at 54°) is pressed from the of the *Linum usitatissimum*, which yield about one-fifth of weight of it. It has a slight peculiar odour, is of a yellow co and remains liquid till within a few degrees of 0°. Owing powerful drying properties, which are much increased after he it with a small quantity of litharge or of peroxide of mangan is extensively used as a vehicle for mixing with colours for p ing in oil: it is also largely employed in the preparation of pri ink, in the preparation of black enamel for leather, and i varnishing of oiled silk. If exposed for some time to a high perature it becomes converted into a dark tenacious mass, when cold may be drawn out into threads; in this state, if m with charcoal, it constitutes printer's ink. If the tenacious m obtained by heating the oil be boiled for some hours with d nitric acid, it acquires a consistence resembling that of ord lead plaster, and becomes hard on exposure to the air; softens again by the heat of boiling water, and acquires a co tence resembling that of caoutchouc, for which it has been tuted in some instances. This *caoutchouc of oils* is soluble of turpentine, in bisulphide of carbon, and in dilute alkaline tions; on neutralizing these alkaline solutions of the caout by means of an acid, the caoutchouc is precipitated una Other drying oils besides linseed oil yield a similar subst though less abundantly.

The oleic acid furnished by the saponification of linsee differs from ordinary oleic acid; Sacc terms it *linoleic acid*, assigns to it the formula ($HO,C_{44}H_{35}O_{8}$). It absorbs o from the air, even when combined with oxide of lead and bases.

Sperm oil (*sp. gr.* 0·868) is the liquid portion of the fat of ermaceti whale. It is of a yellow colour, and has a pecu- sagreeable odour and taste, due to the presence of a small ty of a peculiar oil, termed *phocenin* by Chevreul; this body saponified yields glycerin, and a volatile acid, apparently al with the valeric. The other constituents of the oil are rin and olein. The olein contained in sperm oil differs hat of olive oil, since, although it becomes solid under the of peroxide of nitrogen, it possesses a drying quality. Sperm omes semisolid at about 45°. It may be purified by agitat- o parts of the oil with a mixture of 4 parts of chloride of nd 12 of water; a small quantity of decoction of oak bark wards added to remove traces of a gelatinous matter which ins, and the mixture is left to settle; the clear oil is after- agitated with a small proportion of sulphuric acid, again d by subsidence, and washed to remove adhering sulphuric

Ordinary *whale oil* (*sp. gr.* 0·927) is of a darker yellow colour, s a more disagreeable odour than the foregoing oil. It ot become solid above 32°.

Cod liver oil (*sp. gr.* 0·928) has recently acquired impor- rom its extensive employment as a therapeutic agent. It is ed from the liver of the *Gadus morrhua*, or common cod Its colour varies from a pale, scarcely perceptible yellow, to brown, according to the mode of its extraction. It has a r fishy odour and taste. In addition to the usual compo- f the fish oils, it appears to contain a compound of acetic ith glycerin (acetin, 1069); it also contains a certain pro- of the constituents of the bile, and a small quantity of phorized fat, besides minute quantities of iodine and bro- n a state of combination with some organic substance. dissolves the oil without difficulty, but cold alcohol takes up small quantity of it. The iodine and bromine are not in n of a metallic iodide or bromide; indeed, their presence be detected until the oil has been saponified and the soap . When a drop of concentrated sulphuric acid is allowed into the oil, it produces a beautiful crimson colour, owing ction of the acid upon the biliary matter present.

Castor oil (*sp. gr.* 0·969) is obtained from the seeds of the *communis*; it forms a connecting link between the drying n-drying oils, since it gradually becomes hard by long exposure to air. Castor oil has an acrid taste, which it is stated be removed by agitation with magnesia. This oil is of a viscid consistence, but it does not become solid even at a te rature of 0° F. Castor oil differs from the other fixed oi being soluble in alcohol in all proportions. The principal obtained by its saponification is a modification of oleic acid, te *ricinoleic* acid ($HO,C_{36}H_{33}O_5$), which remains fluid at a temper considerably below 32°. By the action of peroxide of nitrog becomes converted into a solid isomeric fat, termed *ricinelaidi palmic* acid. When treated with ammonia, castor oil yield solid crystalline amide, *ricinolamide* ($C_{36}H_{35}NO_4$). The oil, distilled, furnishes œnanthylic acid ($HO,C_{14}H_{13}O_3$; 1117), a large quantity of the aldehyd of this acid ($C_{14}H_{14}O_2$; 1083), w was termed œnanthol by Bussy. When castor oil is distilled hydrate of potash it is decomposed, the principal products sebacic acid (1135), which remains in the retort, whilst hyd gas is liberated, and a quantity of a volatile liquid (octylic or ca alcohol mixed with caprylic aldehyd), is distilled over (1084).

(1053) *The Solid Fats.*—The solid fats of vegetable o which are in most frequent use are cocoa-nut oil, nutmeg bu and palm oil; those of animal origin are butter, suet, lard, maceti, and bees' wax.

Palm oil, nutmeg butter, and cocoa-nut oil, each contain ferent solid fatty acid, which, in combination with the basis of cerin, constitutes the principal portion of the solid part of th

1. *Cocoa-nut oil* is obtained from the *Cocos nucifera.* largely consumed in the manufacture of candles; it is also the preparation of a species of soap employed for washing in water, and hence termed *marine* soap; it fuses at about Cocoa-nut oil is a very complex fat, for it yields not fewer six different acids on saponification. These acids, accordin Georgey, are—

Caproic acid .	$HO,C_{12}H_{11}O_3$	Lauric acid .	HO,C_{24}H
Caprylic acid .	$HO,C_{16}H_{15}O_3$	Myristic acid .	HO,C H
Capric acid .	$HO,C_{20}H_{19}O_3$	Palmitic acid .	HO,C H

Cocoa-nut oil probably also contains oleic acid, since it sebacic acid when distilled.

2. *Palm oil,* which is of a bright orange or golden colour, is produced from the pulp of the ripe fruit of the *guineensis.* The oil is obtained by heating the crushed fr boiling water. It has an agreeable odour resembling th violets. The solid portion of palm oil consists chiefly of a

has received the name of palmitin, and which, when yields palmitic acid ($HO,C_{32}H_{31}O_3$). Palm oil speedily ancid when kept, and, though when fresh it melts at it gradually becomes less fusible, till it remains solid at ure of 100°. This change is due to the spontaneous ion of the palmitin, and the liberation of palmitic acid, influence of an azotised constituent of the fruit, which es the oil in the process of extraction. Palm oil is olorized by exposure to air at a high temperature, but usual to effect this bleaching of the oil by the addition l quantity of sulphuric acid and bichromate of potash. onstitutes an important article of commerce, upwards of ns being annually imported from the western coast of It is consumed in immense quantities in the manufacture and of soap.

tter consists of a mixture of several fats, amongst which is the principal solid constituent; the olein was considered eis to be of a peculiar kind, which he termed *butyrolein;* lieb has shown that the difference in properties between acid obtained by Bromeis from butter, and that obtained inary olein, depended simply upon the oxidation which it rgone during the process adopted in preparing it; and procured pure oleic acid from butter. According to he solid portion of butter contains, in addition to palmitic ther acid, termed by him *butic acid*, $HO,C_{40}H_{39}O_3$. The istic odour and flavour of butter are owing to the presence ll quantity of some peculiar fats, viz., butyrin, caproin, ylin; each of these fats, when saponified, yields glycerin, culiar volatile acid, viz., butyric acid $HO,C_8H_7O_3$, caproic $,C_{12}H_{11}O_3$, and caprylic acid $HO,C_{16}H_{15}O_3$.

rtain instances Lerch found no butyric or caproic acid in ut in their stead he discovered an acid, which he has the *vaccinic* ($HO,C_{20}H_{19}O_5$). This acid contains the of 1 equivalent of hydrated butyric acid and one of hyproic acid, minus 2 equivalents of oxygen:—

$$\overbrace{,C_{20}H_{19}O_5)}^{\text{inic acid.}}+O_4 = \overbrace{2\,(HO,C_8H_7O_3)}^{\text{Butyric acid.}} + \overbrace{2\,(HO,C_{12}H_{11}O_3.)}^{\text{Caproic acid.}}$$

n of vaccinate of baryta, when exposed to the air, absorbs nd thus becomes converted into a mixture of butyrate ate of this base.

rd is the soft fat of the pig, in which the olein predomir the margarin and stearin.

5. *Suet* is the fat of the ox or of the sheep; when melted it forms tallow. Mutton suet is of a firmer consistence th that from the ox; its solid portion consists almost exclusiv of stearin.

(1054) SPERMACETI (*sp. gr.* 0·940) is the the solid crystalli fat which is extracted from the brain of the spermaceti whale; is accompanied by a fluid oil (sperm oil). Spermaceti differs fr the ordinary fats in not yielding glycerin when saponified, but furnishing in its stead a different base, termed *ethal* ($C_{31}H$ Pure spermaceti, or *cetin* ($C_{64}H_{64}O_4$), fuses at about 120°, solidifies to a silky semitransparent crystalline fat of delicate wh ness. It is insoluble in cold alcohol of sp. gr. of 0·816, bu soluble in hot anhydrous alcohol, and is freely soluble in hot eth from which it crystallizes on cooling. It is acted on with di culty by an aqueous solution of potash. If subjected to distillatio it is decomposed: a liquid hydrocarbon, $C_{32}H_{32}$, called *cete* *cetylene*, passes over, and ultimately palmitic acid (the ethali Dumas, $HO,C_{32}H_{31}O_3$) distils over.

The same acid is formed when spermaceti is fused with half weight of hydrate of potash at a heat of about 220°. Under th circumstances, the mass, which is at first fluid, gradually solidi When this has occurred, it must be treated with water, decomposed by hydrochloric acid: the fatty mass is boiled lime, and then treated with alcohol; palmitate of lime rem undissolved, whilst the new fatty base, ethal, is recovered evaporation. It is purified by redissolving it in ether and eva rating.

Ethal ($C_{32}H_{34}O_2=C_{32}H_{33}O,HO$) is a white solid, fusible 118°. It is soluble in hot alcohol, and crystallizes in plates cools. It may be volatilized by heat without experiencing de position. If distilled with anhydrous phosphoric acid, it y *cetene* $C_{32}H_{32}$, a hydrocarbon homologous with olefiant gas. possesses the properties of a true alcohol; it stands in the relation to palmitic acid as alcohol does to acetic acid; example:—

$$\overbrace{C_4H_5O,HO}^{\text{Alcohol.}}+O_4=\overbrace{HO,C_4H_3O_3}^{\text{Acetic acid.}}+H_2O_2;$$

$$\overbrace{C_{32}H_{33}O,HO}^{\text{Ethal.}}+O_4=\overbrace{HO,C_{32}H_{31}O_3}^{\text{Palmitic acid.}}+H_2O_2.$$

When the vapour of alcohol is passed over heated hydrat potash, hydrogen escapes, and acetate of the base remains beh ethal, under similar treatment, also evolves hydrogen, and uces palmitate of potash :—

$$\overbrace{C_4\,H_5\,O,HO}^{\text{Alcohol.}}+\overbrace{KO,HO}^{\text{Hydrate of potash.}} = \overbrace{KO,C_4\,H_3\,O_3}^{\text{Acetate of potash.}}+2\,H_2;$$

$$\overbrace{C_{32}H_{33}O,HO}^{\text{Ethal.}}+\overbrace{KO,HO}^{\text{Hydrate of potash.}} = \overbrace{KO,C_{32}H_{31}O_3}^{\text{Palmitate of potash.}}+2\,H_2.$$

h sulphuric acid it forms a coupled acid, the *sulphocetic* $O,C_{32}H_{33}O,S_2O_6$), which corresponds with sulphethylic acid. *etylic ether* $(C_{32}H_{33}O)_2$ has also been obtained, spermaceti ng, in fact, a compound of this body with palmitic acid, or a mitate of oxide of cetyl $(C_{32}H_{35}O,C_{32}H_{31}O_3)$, and a homologue etic ether $(C_4H_5O,C_4H_3O_3)$. Spermaceti, when oxidized by ic acid, yields œnanthylic, adipic, and pimelic acids, and a e quantity of succinic acid.

(1055) Bees' Wax (*sp. gr.* 0·96) has been the subject of nume- investigations, but its true nature appears at length to have n satisfactorily explained by Brodie (*Phil. Trans.*, 1848, 1849). ny vegetables produce substances in appearance greatly resem- g the wax furnished by the honey-bee, but these bodies have been thoroughly examined. Bees, even though fed upon pure r only, have the power of converting it into wax, which is efore to be regarded in the light of an animal secretion. wax, at ordinary temperatures, is tough and solid: it has a ow colour, a peculiar smell, and an unctuous feel; it fuses at at 145°. When exposed in thin slices to the air it becomes ched, and is then somewhat less fusible. It may also be ched by means of nitric acid; but chlorine, though it destroys colour, cannot be employed for this purpose with advantage; t was observed by Gay Lussac that a substitution of chlorine a portion of hydrogen occurs under these circumstances, and n candles made from such wax are burned, irritating vapours ydrochloric acid are evolved.

Wax consists of three different substances, which may be par- y separated from each other by means of alcohol. These bodies 1. *Myricin*, which is insoluble in boiling alcohol; 2. *Cerin*, rotic acid, which is dissolved by boiling alcohol, but crystal- out on cooling, and, 3. *Cerolein*, which is retained in the alcoholic liquid.

Cerolein, the substance soluble in cold alcohol, is a greasy , to which the colour, odour, and tenacity of the wax are it has an acid reaction; it fuses at about 83°, and is readily soluble in ether: but it has been only incompletely examined constitutes not more than 4 or 5 per cent. of the wax.

Cerotic acid ($HO,C_{54}H_{53}O_3$; Brodie) is extracted from by means of boiling alcohol, and is purified by recrystalliz from alcohol until its melting point rises to 162° F. It is th recrystallized from ether until it fuses at 174°, which is the ing point of the pure acid. The proportion of free cerotic contained in wax varies in different samples. In a specimen Ceylon it was entirely wanting. In a sample of genuine bees' operated on by Brodie, the cerotic acid constituted about per cent. of the wax.* If due care be taken, cerotic acid may distilled without undergoing decomposition.

Myricin.—The portion of the wax insoluble in alcohol stitutes upwards of two-thirds of the bulk of ordinary bees' It melts at 147°. It is a mixture of two different bodies, bot which are insoluble in alcohol, but soluble in ether; a p crystallizes from the ethereal solution in feathery scales repeated crystallization from ether a substance may be obt which solidifies at 162° F. To this substance the name of cin is confined by Brodie. The other more fusible body accompanies it is less abundant, and has not been compl investigated. Purified myricin, when fused with hydrate of p or when boiled with an alcoholic solution of potash, is saponified; by this means a salt of palmitic acid is obtained, another wax alcohol, *melissylic* alcohol, or *melissin* ($C_{60}H_{61}O$,H is liberated. From this decomposition it appears that my is a body analogous to spermaceti and to Chinese wax; myricin being a *palmitate of oxide of melissyl*, ($C_{60}H_{61}O,C_{32}H$ or ($C_{92}H_{92}O_4$).

Melissin fuses at 185°. It is soluble with difficulty boiling alcohol. It crystallizes from a hot solution in satiny crystals. Benzol is a better solvent for it than alcohol or ether. When melissylic alcohol is distilled with hydrate of potash, it is decomposed, hydrogen is evolved,

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* Chinese wax ($C_{108}H_{108}O_4$), the produce of a species of ins coccus tribe, contains cerotic acid in a state of combination with cerotyl, forming a substance which fuses at 182°, and is homolog spermaceti, which in its crystalline appearance it considerably rese

$$\overbrace{C_{32}H_{33}O,C_{32}H_{31}O_3}^{\text{Spermaceti.}} \quad : \quad \overbrace{C_{54}H_{55}O,C_{54}H_{53}O_3}^{\text{Chinese Wax.}}.$$

Chinese wax, when decomposed by fusion with hydrate of potash, cerotate of potash; and at the same time *cerotin* ($C_{54}H_{55}$)H,O_2, the cerotic acid (corresponding to the ethal of spermaceti) is obtained.

issate of potash is formed; the reaction being analogous to that which acetate of potash is produced when ordinary alcohol is ated in a similar manner:—

$$\overbrace{C_{60}H_{61}O,HO}^{\text{Melissin.}}+KO,HO=\overbrace{KO,C_{60}H_{59}O_3}^{\text{Melissate of potash.}}+2\,H_2.$$

lissic acid, it will be seen, is the homologue of acetic acid, and longs to the series of acids, $HO,(C_{2n}H_{2n-1})O_3$; it fuses at 192°, and may be volatilized without decomposition.

Wax, when submitted to distillation, yields several solid hydrorbons, among which is *melene* ($C_{60}H_{60}$), which fuses at 143°·6. e principal product of the oxidation of wax by means of nitric d is succinic acid.

From the foregoing statements it appears, therefore, that bees' x is a mixture of cerotic acid (cerin) with palmitate of melissyl yricin), in addition to which is a portion of a third body allied myricin, as yet but imperfectly examined; with a small quantity a soft greasy substance, cerolein. The following well-defined bstances may be enumerated as derivatives from wax:—

	Fusing point.	Formula.
Cerotic acid (*cerin*)	174° .	$HO,C_{54}H_{53}O_3$
Cerylic alcohol (*cerotin*) . .	177°·8 .	$C_{54}H_{55}O,HO$
Chinese wax	182° .	$C_{108}H_{108}O_4$
Cerene (*paraffin*)	135° .	$C_{54}H_{54}$
Melissylic alcohol (*melissin*).	185° .	$C_{60}H_{61}O,HO$
Melissic acid	192° .	$HO,C_{60}H_{59}O_3$
Palmitic acid	143°·6 .	$HO,C_{32}H_{31}O_3$
Myricin	162° .	$C_{92}H_{92}O_4$
Melene (*paraffin*)	143°·6 .	$C_{60}H_{60}$.

(*b*) *Proximate Constituents of the Fats and Oils.*

(1056) From the preceding general description of the oils and , it is evident that these bodies contain several distinct subnces, which are analogous to each other in chemical composition. e most important of these neutral fats are stearin, palmitin, rgarin, and olein.

(1057) **Stearin** ($C_{114}H_{110}O_{12}$; Berthelot) is a white crystalline , soluble in about seven times its weight of boiling alcohol, d much more freely so in hot ether. Nearly the whole of stearin separates from these liquids as they cool. Duffy *J. Chem. Soc.*, v. 210) finds that stearin may exist in three ifications, each of which has a different fusing point. Under ordinary circumstances, the melting point is 144° F., but this temperature varies in a remarkable manner under the influence of slight differences of the temperature to which the stearin is exposed during the act of fusion:—1. If stearin be heated to 151°, and allowed to cool, it remains liquid till it reaches 124°, and after solidification it may be melted at 125°·6;—2. but if stearin, which has been melted at this temperature, be again allowed to solidify, it requires a temperature of 147°·4 for its liquefaction; —and 3. stearin, which has been melted at 144°, and the temperature of which has not been raised beyond 147°, solidifies at 141°·8, but after solidification it requires a temperature of 157° for its liquefaction. These three modifications of stearin have different densities:—

	Sp. gr.
1. Modification α, fusible at 125°·6 .	0·986
2. Modification β, fusible at 147°·4 .	1·010
3. Modification γ, fusible at 157° .	1·017*

Similar modifications are produced by heat upon palmitin.

Stearin is the most abundant of the solid constituents of the fats and fixed oils. It is generally prepared from mutton suet, in which it is mixed with but small quantities of other fats: the suet is heated with about ten times its volume of ether; when it cools, the olein and margarin are held in solution, while the stearin crystallizes in pearly scales. These must be pressed between folds of blotting paper, redissolved in ether, and recrystallized until the melting point becomes constant.

Berthelot has succeeded in preparing stearin artificially, by heating stearic acid and glycerin together in closed vessels for several hours under pressure. He has also obtained all the other neutral fats by similar means (1069).

(1058) PALMITIN ($C_{102}H_{98}O_{12}$; Berthelot).—This fat is contained abundantly in palm oil, from which it has received its name. It is extracted from the oil by first pressing out the liquid portion, treating the residue with boiling alcohol to remove free palmitic acid, and then crystallizing repeatedly from ether. According to Duffy the lowest point at which palmitin remains liquid is 113°·9; but it has three different melting points, viz.—114°·8, 143°, and 145°, which correspond to three different modifications like those of stearin. Palmitin is also present in bees' wax, in cocoa-nut oil, and (according to Heintz) in human fat. The tree wax of Japan consists of pure palmitin (Sthamer).

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* Heintz, on repeating Duffy's experiments upon pure stearin prepared synthetically by Berthelot's process (1069), obtained only the varieties α and γ; Duffy's β he considers to have been produced from the presence of a slight impurity in the stearin. The fusing points given by Heintz are a little higher than those of Duffy—viz., for α 131°, and for γ 160°·8.

(1059) MARGARIN ($C_{108}H_{104}O_{12}$; Berthelot) crystallizes in pearly scales, which are fusible at about 116°. It requires about 400 times its weight of boiling alcohol for solution, and is deposited almost entirely on cooling. Margarin constitutes the solid ingredient of goose grease, of human fat, and of olive oil. It may be extracted from olive oil by lowering its temperature to 32°, and then submitting it to pressure; the solid portion is again melted and cooled slowly, and a second time submitted to pressure, at a temperature of from 55° to 60°. After two or three crystallizations from boiling alcohol, the margarin is obtained nearly pure.

According to Heintz, margarin is not a simple fat; for when saponified, the acid which it yields, and which is commonly described as margaric acid, admits of separation into palmitic and stearic acids; hence what is called margaric acid appears to be a mere mixture of these acids (1122).

(1060) OLEIN ($C_{114}H_{104}O_{12}$; Berthelot).—Pure olein is colourless; it is not solidified by a cold of 32°. By exposure to the air it absorbs oxygen slowly, with evolution of carbonic acid, and becomes resinoid in appearance. Olein when distilled gives rise, amongst other products, to the formation of sebacic acid (2 HO, $C_{20}H_{16}O_6$), which is a characteristic product of the destructive distillation of oleic acid. Peroxide of nitrogen converts olein into an isomeric solid fat, which has received the name of *elaidin.* Subnitrate of mercury which has been prepared without the aid of heat, retains a sufficient quantity of peroxide of nitrogen to enable it, when placed in contact with olein, to convert it into elaidin; and it produces a similar effect upon all oils which contain that variety of olein which is present in the non-drying oils. The drying oils contain a form of olein which does not become solid when mixed with subnitrate of mercury; hence this salt has been employed in testing olive oil suspected to have been adulterated with poppy and other cheap drying oils. The oil is agitated with $\frac{1}{12}$th of its weight of a solution of the subnitrate; the purer the oil the more rapidly does it become solid when thus treated.

The purification of olein is attended with considerable difficulty: it may however be obtained either by solidifying olive oil at a temperature of 32° and pressing out the liquid portion, or by dissolving the oil in boiling alcohol, which, as it cools, depo nearly the whole of the stearin and margarin, but retains the wh of the olein in solution: the olein may then be recovered b driving off the alcohol by heat. Olein is saponified with great difficulty than the solid fats which accompany it, and it has be proposed to apply this circumstance to its purification. If oli oil be boiled for twenty-four hours with a solution of caustic so of moderate strength, containing a quantity of alkali equal to abo half that required for the complete saponification of the oil, th olein remains unchanged, whilst the solid fats are saponified. Th mixture of soap and olein is treated with dilute alcohol, whi dissolves the soap, while the olein collects as an oily layer upo the surface.

It has been already mentioned that the liquid portion of th oils has not the same composition throughout the different varieti of these substances: the olein of olive oil differs from the ole of linseed oil, or *linolein;* and both of these differ from the ole contained in castor oil.

Adipocire is the name which has been given to a fatty resid which is often obtained from the slow decay of the bodies of m or of animals which have been interred in a soil which is ke constantly moist. Wetherill (*Liebig and Kopp*, *Jahresb.* 1855, 51 finds it to consist chiefly of solid fatty acids free from cholester from ammonia, and from glycerin, so that it is most probably th result of the gradual decomposition of fat originally present in th body, from which, during the decay of the muscular tissue, must the glycerin and oleic acid have been removed.

(*c*) *Action of Bases upon Fatty Matters.—Soap-making*

(1061) It is well known that however thoroughly water an oily matters may be incorporated by mixture, they do not unite form a homogeneous compound; but that after a short time th grease separates and floats upon the surface. If, however, a qua tity of a solution of caustic soda be added to the mixture, and be then agitated, a milky-looking fluid or emulsion will be form and the oil will remain mixed with water.

If a sufficient quantity of alkali be added, this emulsion wh boiled for some hours gradually becomes clear; and a period arri at which a transparent ropy fluid is formed, which froths stron on agitation, and presents the characters of a concentrated solutio of soap.

If to a portion of this clear liquid a strong solution common salt be added, a curdling is immediately produced: the liquid separates into a clear solution which retains the glycerin, whilst a granular substance rises to the surface: this substance, if drained, pressed, and dried, exhibits the properties of soap.

Ordinary soap is freely soluble in hot water, forming with it a transparent solution, which, if tolerably strong, becomes a white opaque jelly as it cools: soap may also be dissolved by hot alcohol, which as it evaporates leaves the soap in transparent blocks. It is quite insoluble in strong brine, and in a concentrated solution of caustic potash or of soda; hence by the addition of chloride of sodium, or of caustic alkali, to a solution of soap, the soap is separated from the liquid in the solid form.

(1062) *Varieties of Soap.*—There are various kinds of soap, dependent on the nature of the fat, as well as upon that of the base used in its preparation. The base of the ***hard soaps*** is soda, that of the ***soft soaps*** is potash. The common soft soaps have always a more powerfully alkaline reaction than the hard soaps, owing to the presence of an excess of alkali, which adds to their detergent power; they also usually contain the glycerin of the fat, which the manufacturer has not been at the pains to separate. If the oil be heated with oxide of lead, instead of with alkali, a white, solid, fusible compound, well known as *lead plaster*, is formed; which is, in fact, a soap containing oxide of lead as its base, instead of soda or potash. The earths if boiled with the oils also produce soaps; but such soaps are insoluble in water, and it is owing to the formation of these compounds that the *curdling* of soap by *hard* water is occasioned. Now, hard waters are waters which contain a certain quantity of earthy salts—usually of lime or of magnesia. When ordinary soap is dissolved in these waters, double decomposition occurs, the lime displaces the alkali in the soap, and the alkali in turn combines with the acid which was previously united with the lime; and the insoluble lime soap thus formed, produces the curdling in question.

The soaps of the alkalies, or commercial soaps, are the only ones which are soluble in distilled water as well as in alcohol and in ether; but alcohol dissolves many of the compounds which the fatty acids form with the oxides of copper, iron, and manganese. Oil of turpentine and the fixed oils likewise dissolve small quantities of these soaps.

(1063) *Process of Soap-making.*—The unctuous materials which are used in this country in the preparation of hard soap are, tallow, *which gives the hardest soap*, palm oil, and kitchen grease: rosin is also an ingredient in yellow soap. The coarse soft soaps are made of common fish oil and hemp-seed oil.

The manufacture of soap is carried on in large iron boilers called *coppers,* in which the mixture of ley and fat is heated by means either of an open fire, or of steam: the steam is either admitted into the copper by a perforated pipe, or it is made to circulate within it through a closed coil or worm. For hard soaps the leys of caustic soda are prepared in large iron vats, which are also heated by steam. Water is put into the vat and made to boil; a mixture of soda ash and slaked lime is then added in quantity sufficient to make the ley of the sp. gr. of 1·15; after boiling for some time the steam is turned off, the carbonate of lime allowed to subside, and the clear ley is drawn off. Fresh water is added to the residue, and thus a weaker ley is obtained.

Mottled soap is prepared from tallow, palm oil, and kitchen stuff. For every ton of tallow or fat introduced into the boiler, about 150 gallons of partly exhausted soda ley is added from a previous charge. When it first boils, a milky liquid is formed, which by degrees becomes more and more viscid; strong leys are then gradually added, and the boiling is continued until the soap ceases to feel greasy. A quantity of common salt is next added to separate the spent leys; these contain the glycerin and some impurities derived from the grease; they are drawn off from the bottom, and are thrown away. Strong ley is then added, and the boiling continued, until the soap separates from the ley, which retains an excess of alkali. It is then *cleansed* or transferred to the soap frames to cool. These frames are rectangular in shape, and consist of cast-iron plates cramped together by bolts and nuts; in these frames a small portion of the ley contained in the hot soap gradually separates, and accumulates in the lower part of the frame; this part of the soap is pared off, and is re-melted and added to the next charge. The soap remains in the frames for four or five days to cool and harden. At the end of that time it is cut up with wires into bars.

The *mottling* occurs in the moulds spontaneously, and is due to the separation from the mass of a small portion of iron soap, which gradually arranges itself in blue veins. This mottling is chiefly prized as a test that the soap is not too moist; since if too large a proportion of water were present, the colouring matter would sink to the lower part of the frame and accumulate there. Good soap contains about 30 per cent. of water; and 100 parts of fat or oil yield from 150 to 155 of such soap. A soda soap, before drying, contains about 6 or 7 per cent. of alkali.

Curd soap is usually obtained from tallow only, a small por-n of olive oil or of lard being sometimes added. The soap ile hot is put into a pan and *crutched*, or stirred forcibly, to ak up the grain; it is then conveyed to the frames. When it should be perfectly smooth and white. *Yellow* soap is de from tallow and palm oil, and in addition to the alkali and contains a considerable proportion of common rosin, which sesses acid properties and unites with the alkali: it is manu-ured by a process similar to that used for mottled soap, but ead of being *cleansed*, or put into the frames immediately after ing, it is *fitted*, or mixed in the copper with a small quantity water, which in two or three days carries down the excess of ali, forming the *negur*, which subsides to the bottom; while a ngy crust, termed the *fob*, rises to the surface. The fob is mmed off, and the semi-solid pasty mass of soap is trans-red to the frames. The negur and fob are added to the next il.

Marseilles and Castile soaps are made from olive oil and soda; y are mottled by the addition of green vitriol and sulphuretted to the soap while in the pasty state.

(*d*) *Manufacture of Fatty Acids for Candles.*

(1064) Large quantities of the fats are converted into the form free acids, in the manufacture of what are often incorrectly ed stearin candles. This branch of industry has within the few years acquired enormous magnitude. The fatty acids are pared for this purpose by three principal methods;—in the first these processes the fat is saponified by means of lime; in the nd the fat or oil is decomposed by sulphuric acid; and in the rd process the fat is separated into glycerin and the fatty acid, der the influence of water at an elevated temperature. The acids nished by the fats are, at ordinary temperatures, whiter and der than the fats from which they are obtained, and they are the same time cleaner and more combustible.

1. *Saponification by Lime.*—Until recently it was the general ctice to saponify the oils or fats by means of lime, which readily cts the desired change, and has the advantage of being much per than either potash or soda: this process is still exten-ly followed in France. The tallow is melted by injecting hot m into the vat which contains it, and milk of lime is added; the le being maintained at the temperature of 212° by continually ting steam through a perforated pipe, whilst the mixture is

kept constantly stirred. An insoluble lime soap is thus formed it is drained from the solution of glycerin, and then decomposed by the cautious addition of sulphuric acid diluted to th sp. gr. 1·160. The melted fatty acids thus rise in the for of an oil to the surface of the heated mixture; they are no decanted, and are washed, first with a fresh portion of heated dilu sulphuric acid, and afterwards with water. The fused acids ar then cast into thin plates or cakes not much exceeding an inch i thickness; these cakes when cold are placed between layers o cocoa-nut matting, and are piled up one above another with iro plates interposed between every four or five cakes, and the pi thus formed is subjected to intense pressure by the aid of powerful hydraulic press. By this means the oleic acid is in gre measure forced out, whilst the harder palmitic and stearic ac remain, and are afterwards subjected to pressure at a higher temperature; a fresh portion of the more fusible fat is removed by th operation, and the residue becomes beautifully white. In order t remove any traces of oxide of iron which the fat may have absorb from the machinery, it is again washed, first with warm dilute sulphuric acid, then with water, and finally is melted and mould into candles. The oleic acid furnishes with soda a soap sufficiently hard to be used for many purposes in the arts.

M. Milly has ascertained that the complete saponification fats may be effected by a proportion of lime not exceeding 4 p cent. of the weight of the fat, by exposing the mixture, in a Pap digester, with water to a high temperature. This temperat according to Pelouze, need not be higher than from 311° to 3 If water alone be employed to effect the decomposition, a temperature of not less than 428°, prolonged for many hours, is need

(1065) 2. *Acidification of the Fats by Sulphuric Acid.*—T action of sulphuric acid upon the fixed oils has been particul examined by Fremy (*Ann. de Chimie*, II. lxv. 113). When concentrated sulphuric acid is made to act at ordinary temperat upon an oil or fat, the fat at first combines with the acid, and t compound thus formed gradually becomes decomposed into sulphoglyceric (1068), *sulpholeic*, *sulphopalmitic*, and *sulphostearic* a The last three sulpho-acids are insoluble in acidulated water, b are dissolved by pure cold water. They have an oily bitter ta On raising the temperature of the solution they become decomposed, the sulphuric acid is set at liberty, and the glycerin and t fatty acids are separated. The sulpholeic acid is more perm than the sulpho-compounds of the solid fatty acids.

If the sulphuric acid and the oil or fat be made to act u each other at a high temperature, the fat is immediately broken up into glycerin and the fatty acids, whilst the glycerin is in its turn decomposed, at the expense of a portion of the sulphuric acid, and sulphurous and carbonic acids are evolved. This reaction is employed on a large scale for the preparation of the so-called composite or stearine candles, and in England it has very nearly superseded the lime process.

The following is an outline of the method in which sulphuric acid is applied for this purpose by Messrs. Wilson at the works of Price's Patent Candle Company :—The fat is first melted and freed from impurities, then mixed with from one-twelfth to one-seventeenth of its weight of oil of vitriol in large copper boilers, where it is raised gradually by means of a current of highly heated steam to a temperature of about 350°. This temperature is maintained for about two hours, the mass being frequently stirred briskly; during this process carbonic and sulphurous acids are disengaged in large quantities, nearly all the glycerin and sulphuric acid being decomposed in the course of the operation. The liberated fatty acids are of a dark colour, and require thorough washing with water to free them from adhering sulphuric acid.

The impure fatty acids thus obtained are then subjected to distillation, which is effected by placing them in a copper vessel, into the lower part of which a current of steam at the ordinary pressure is injected; previous to its admission to the still this steam is heated to about 600°, by transmitting it through pipes heated nearly to redness. The distillation does not take place below 400° F., but towards the latter part of the process the temperature frequently rises to 500°. After the acidified fats have been distilled as far as is advantageous, the dark residue in the retort may yet be made to yield a considerable amount of fat by submitting it to pressure; the black solid mass which still remains is used as fuel. The distilled fat is broken up into fragments, and distributed in layers of about three-fourths of an inch in thickness upon squares of cocoa-nut matting, which are piled one above another, and submitted to the action of a hydraulic press. The fat thus obtained is sufficiently firm to be made at once into candles suited to European climates, but for the Indian market it is necessary again to subject the fat to pressure, which this time is effected at a temperature of 120°.

(1066) 3. *Action of Water at a high temperature on Fats and Oils.*—Mr. Tilghmann a few years ago made the important observation, that when a mixture of fat and water is forced under strong pressure through tubes heated nearly to redness, so a raise the temperature of the mass to 400° or 500°, the fa entirely decomposed into glycerin and fatty acids; the element water enter into combination with those of the fat, so that by means a result is obtained exactly the reverse of that effected Berthelot at lower temperatures (1069), when the acid and glyc are digested together.

Mr. Wilson by injecting superheated steam at a tempera of between 500° and 600° into heated fat, was able to produc similar separation of hydrated glycerin and of the acids with w it was previously in combination, and at the same time he ceeded in effecting the distillation, not only of the fat, but als the glycerin; the latter is thus obtained in a high degree of centration, as a beautiful, colourless, syrupy liquid, which ca prepared in almost unlimited quantity. The fatty acids are procured by the same operation in a very pure form, so that process, from its simplicity, and from the purity of the prod which it yields, bids fair to supersede those previously empl in the preparation of the fatty acids for illuminating purp The operation, however, cannot be conducted so rapidly as process of decomposition by sulphuric acid.

§ II. GLYCERIN.—THE GLYCERIDES.

(1067) GLYCERIN ($C_6H_8O_6$), *the Sweet principle of Oils*; *gr.* 1·28 at 59°.—This substance is separated from all fatty oily bodies (with the exception of spermaceti and the diff varieties of wax), during their saponification by alkalies. Acc ing to Pasteur it is also formed in small quantities during process of alcoholic fermentation. Glycerin is a viscid, colou liquid of a sweet taste, soluble in water and alcohol in all pro tions, but sparingly soluble in ether. It dissolves most of deliquescent salts, as well as many other substances which soluble in water. Baryta, lime, and strontia are freely sol in glycerin, and the solutions are not precipitated by carb acid. Glycerin is slightly volatile at 212°, but, if distilled al the greater part of it experiences decomposition; intensely pun vapours of acrolein ($C_6H_4O_2$; 1071) are then disengaged, w excite a most painful irritation of the eyes. When heated s ciently in air, glycerin burns with a luminous flame. It c however, be distilled without alteration, in a current of s heated steam which has been raised to a temperature of betw 500° and 600°; advantage is taken of this fact in order to pr glycerin in large quantities (1066). The usual method of o

erin on a small scale consists in saponifying olive oil by
it with an equal weight of litharge: the oxide of lead is
ith water and added to the oil, with which it is boiled till
nification is complete; fresh portions of water being added
ne to time to supply the place of that which is evaporated.
cerin is dissolved by the water, and is easily freed from
luble *lead plaster*, or mixed oleate and margarate of lead
formed. The aqueous solution retains a small quantity
of lead, which may be separated by transmitting through
ent of sulphuretted hydrogen, and filtering from the pre-
sulphide of lead; the water may then be expelled by
ion *in vacuo* at a temperature not exceeding 300° F. If
tion be evaporated in the open air, it becomes brown.
forms a valuable preservative liquid in which small and
tissues may be mounted for anatomical purposes. Like
possesses strong antiseptic powers, and has been applied
g meat. It also forms a useful application to the surface
kin when dry and irritable.

the alcohols in general glycerin forms the following series
atives:—

Combinations with acids, corresponding to the compound
such as the natural and artificial fats.

Combinations with alcohol radicles, corresponding to the
thers, such as diethylin (1070).

A compound corresponding to the simple ethers, such as
ether.

Hydrocarbons, such as tritylene.

Combinations with ammonia analogous to the ethylic

Oxidized derivatives, corresponding to the aldehyds.

Other oxides, possessing acid properties, such as glyceric

en glycerin is heated with hydrate of potash, it is decom-
nto a mixture of acetate and formiate of potash, whilst
n escapes:—

$$+ 2\,(HO,KO) = \overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}} + \overbrace{KO,C_2HO_3}^{\text{Formiate of potash.}} + H_2O_2 + 2\,H_2.$$

ligesting glycerin for some weeks at a temperature of 100°F.,
or cheese in contact with chalk, it may be made to fur-
ohol, the amount of which never exceeds one-tenth of
ht of glycerin employed, the greater part of the glycerin
unaltered in the liquid; equal volumes of carbonic

acid and of hydrogen being disengaged during the process; (Berthelot); ($C_6H_8O_6 = C_4H_6O_2 + C_2O_4 + H_2$).

According to Redtenbacher (*Liebig's Annal.* lvii. 174), if a dilute solution of glycerin be mixed with well-washed yeast, and kept for some weeks at a temperature of from 70° to 85°, water being added as it evaporates, it becomes slowly converted into propionic acid; very little evolution of gas occurs, but the liquid becomes mouldy and acquires an acid reaction: if the mixture be neutralized from time to time with carbonate of soda, and as soon as the further development of acid ceases, the liquid be filtered and evaporated, a yellow saline mass is obtained, possessing the smell of *sauer-kraut:* when this saline mass is distilled after the addition of sulphuric acid, propionic acid is the principal product condensed in the receiver. The connexion between the composition of propionic acid and glycerin is very simple, 1 atom of hydrated propionic acid with 2 atoms of water containing the elements of 1 atom of glycerin:—

$$\overbrace{C_6H_8O_6}^{\text{Glycerin.}} = \overbrace{HO,O_6H_5O_3}^{\text{Propionic acid.}} + H_2O_2.$$

Berthelot found that glycerin, like mannite, was convertible into a true fermentable sugar under the influence of the testicular tissue (945).

Glycerin admits of oxidation without difficulty; if distilled with diluted sulphuric acid and oxide of manganese, formic acid is amongst the products; and under the combined influence of platinum black and atmospheric air it rapidly absorbs oxygen, and yields an acid, the nature of which has not been ascertained.

An interesting series of experiments was made by Berthelot and De Luca, upon the action of biniodide of phosphorus upon glycerin (*Ann. de Chimie,* III. xliii. 257). When equal parts of crystallized biniodide of phosphorus (PI_2) and of glycerin are mixed in a capacious retort, considerable heat is developed; a new compound (C_6H_5I) mixed with water distils over; it is called *iodized propylene,* but the name *iodide of allyl* would be more appropriate (1282); a considerable volume of pure gaseous tritylene (propylene) is also evolved, whilst free iodine and phosphorous acid remain in the retort, mixed with the excess of glycerin employed. The reaction is a remarkable one, for it will be observed that the whole of the oxygen of the glycerin is removed, one portion of it uniting with the phosphorus to form phosphorous acid, and the remaining portion being eliminated with hydrogen in the form of water, whilst the carbon remains in the form of iodide of allyl:—

$$\overbrace{2\,PI_2}^{\text{Biniodide of Phosphorus.}}+\overbrace{2\,C_6H_8O_6}^{\text{Glycerin.}}=\overbrace{2\,C_6H_5I}^{\text{Iodide of Allyl.}}+\overbrace{2\,(2\,HO,PO_3)}^{\text{Phosphorous acid.}}+H_2O_2+I_2.$$

The tritylene which is disengaged is the result of a secondary action, connected probably with the formation of a peculiar iodized compound (? iodhydrin $C_{12}H_{11}IO_6$) which is found in the retort in small quantity.

Glycerin may be reproduced by the decomposition of tribromide of allyl by means of acetate of silver, and the subsequent treatment of the acetate so obtained with hydrate of potash :—

$$\overbrace{C_6H_5Br_3}^{\text{Tribromide of allyl.}}+3\,\overbrace{(AgO,C_4H_3O_3)}^{\text{Acetate of silver.}}=3\,AgBr+\overbrace{C_6H_5O_3,\,3\,C_4H_3O_3}^{\text{Triacetin.}};$$

and

$$\overbrace{C_6H_5O_3.\,3\,C_4H_3O_3}^{\text{Triacetin.}}+3\,(KO,HO)=\overbrace{C_6H_8O_6}^{\text{Glycerin.}}+3\,\overbrace{(KO,C_4H_3O_3)}^{\text{Acet. potash.}}.$$

(1068) *Action of Acids upon Glycerin.*—Nitric acid rapidly attacks glycerin, and converts it into carbonic and oxalic acids. If glycerin be allowed to fall drop by drop into a mixture of equal measures of nitric acid and oil of vitriol, care being taken to prevent the temperature from rising too high, a heavy oily-looking liquid collects at the bottom of the acid. It is powerfully explosive, and detonates either by a blow or by elevation of temperature; a single drop placed upon paper and struck upon an anvil, producing a deafening report. This body is a substitution-compound of glycerin, in which 2 atoms of hydrogen are displaced by an equal number of equivalents of peroxide of nitrogen. It has been termed *nitro-glycerin*, or *glonoin*, [$C_6H_6(NO_4)_2O_6$; De Vry]. It is insoluble in alcohol and in ether; it has a sweetish, pungent, aromatic taste, and if but a single drop be placed upon the tongue, it produces a painful aching in the back of the head, which lasts for many hours.

Glycerin enters like alcohol into combination with many of the polybasic acids, forming compounds analogous to sulphethylic acid. Thus, when oil of vitriol is mixed with half its weight of glycerin, the two bodies unite with considerable evolution of heat: the compound acid forms soluble salts with lime and baryta; the lime salt, according to Pelouze, has a composition which may be represented by the formula ($CaO,\ C_6H_7O_5,\ S_2O_6$), the *sulpho-glyceric* acid saturating only half the quantity of base which would be required by the sulphuric acid which it contains. A compound similar to the foregoing one may be formed with glycerin and phosphoric acid; it is very soluble both in water and in alcohol, but is easily decomposed into free phosphoric acid and glycerin. Phosphoglyceric acid exists ready formed in the yolk of the egg (Gobley), and probably also in the brain.

(1069) *Artificial Formation of Fats.—Glycerides.*—The most important compounds which are produced by the action of acids upon glycerin are the compound ethers of glycerin or the *glycerides,* which are analogous in composition to the various fats and oils. Berthelot has succeeded in forming these bodies by the direct action of the fatty acids upon glycerin, and has not only reproduced several of the natural fats (*Ann. de Chimie,* III. xli. 216), but has also obtained a large class of such bodies which were not previously known. According to the researches of this chemist, stearic, palmitic, and oleic acids each forms three compounds by its union with glycerin; and the act of combination is attended by the separation of water in each case. The following table contains a list of the more important of these compounds, with the formulæ of the decomposition which appears to attend their formation:—

Artificial fats, or Ethers from Glycerin.

			Stearic acid.		Glycerin.		
Monostearin	$=C_{42}H_{42}O_8$	=	$C_{36}H_{36}O_4$	+	$C_6H_8O_6$	−	H_2O_2,
Distearin	$=C_{78}H_{78}O_{12}$	=	$2\,C_{36}H_{36}O_4$	+	$C_6H_8O_6$	−	H_2O_2?
Tristearin	$=C_{114}H_{110}O_{12}$	=	$3\,C_{36}H_{36}O_4$	+	$C_6H_8O_6$	−	$3\,H_2O_2$
			Palmitic acid.				
Monopalmitin	$=C_{38}H_{38}O_8$	=	$C_{32}H_{32}O_4$	+	$C_6H_8O_6$	−	H_2O_2
Dipalmitin	$=C_{70}H_{70}O_{12}$	=	$2\,C_{32}H_{32}O_4$	+	$C_6H_8O_6$	−	H_2O_2
Tripalmitin	$=C_{102}H_{98}O_{12}$	=	$3\,C_{32}H_{32}O_4$	+	$C_6H_8O_6$	−	$3\,H_2O_2$
			Oleic acid.				
Monolein	$=C_{42}H_{40}O_8$	=	$C_{36}H_{34}O_4$	+	$C_6H_8O_6$	−	H_2O_2,
Diolein	$=C_{78}H_{74}O_{12}$	=	$2\,C_{36}H_{34}O_4$	+	$C_6H_8O_6$	−	H_2O_2?
Triolein	$=C_{114}H_{104}O_{12}$	=	$3\,C_{36}H_{34}O_4$	+	$C_6H_8O_6$	−	$3\,H_2O_2$
			Valeric acid.				
Monovalerin	$=C_{16}H_{16}O_8$	=	$C_{10}H_{10}O_4$	+	$C_6H_8O_6$	−	H_2O_2
Divalerin	$=C_{26}H_{26}O_{12}$	=	$2\,C_{10}H_{10}O_4$	+	$C_6H_8O_6$	−	H_2O_2?
Trivalerin	$=C_{36}H_{32}O_{12}$	=	$3\,C_{10}H_{10}O_4$	+	$C_6H_8O_6$	−	$3\,H_2O_2$
			Butyric acid.				
Monobutyrin	$=C_{14}H_{14}O_8$	=	$C_8H_8O_4$	+	$C_6H_8O_6$	−	H_2O_2,
Dibutyrin	$=C_{22}H_{22}O_{12}$	=	$2\,C_8H_8O_4$	+	$C_6H_8O_6$	−	H_2O_2?
Tributyrin	$=C_{30}H_{26}O_{12}$	=	$3\,C_8H_8O_4$	+	$C_6H_8O_6$	−	$3\,H_2O_2$
			Acetic acid.				
Monacetin	$=C_{10}H_{10}O_8$	=	$C_4H_4O_4$	+	$C_6H_8O_6$	−	H_2O_2
Diacetin	$=C_{14}H_{12}O_{10}$	=	$2\,C_4H_4O_4$	+	$C_6H_8O_6$	−	$2\,H_2O_2$
Triacetin	$=C_{18}H_{14}O_{12}$	=	$3\,C_4H_4O_4$	+	$C_6H_8O_6$	−	$3\,H_2O_2$

oicin $=C_{20}H_{12}O_8 = \overbrace{C_{14}H_6O_4}^{\text{Benzoic acid.}} + \overbrace{C_6H_8O_6}^{\text{Glycerin.}} - H_2O_2$

in $=C_{48}H_{20}O_{12} = 3\,C_{14}H_6O_4 + C_6H_8O_6 - 3\,H_2O_2$

$=C_{32}H_{30}O_{16} = \overbrace{C_{20}H_{18}O_8}^{\text{Sebacic acid.}} + 2\,C_6H_8O_6 - 2\,H_2O_2$

hydrin $=C_6H_7ClO_4 = HCl + C_6H_8O_6 - H_2O_2$

drin $=C_6H_6Cl_2O_2 = 2\,HCl + C_6H_8O_6 - 2\,H_2O_2$

drin $=C_6H_5Cl_3 = 3\,HCl + C_6H_8O_6 - 3\,H_2O_2$

drin $=C_6H_5ClO_2 = HCl + C_6H_8O_6 - 2\,H_2O_2$

hydrin $=C_6H_4Cl_2 = 2\,HCl + C_6H_8O_6 - 3\,H_2O_2$

hydrin $=C_{20}H_{11}ClO_6 = \overbrace{C_{14}H_6O_4}^{\text{Benzoic acid.}} + HCl + C_6H_8O_6 - 2\,H_2O_2$

obrom- $\}=C_{10}H_8ClBrO_4 = HCl + HBr + C_4H_4O_4 + C_6H_8O_6 - 3\,H_2O_2$

$=C_{14}H_{16}O_6 = \overbrace{2\,C_4H_6O_2}^{\text{Alcohol.}} + C_6H_8O_6 - 2\,H_2O_2$

ght have been expected that in the formation of these ls the quantity of water separated should have been different, and that the proportions in the three com-hould have been, H_2O_2 in the first, 2 H_2O_2 in the nd 3 H_2O_2 in the third: each equivalent of the hydrated g an atom of water, whilst the single atom of glycerin, of combination, should lose 1, 2, and 3 atoms of water, to the number of equivalents of acid with which it is com-ndeed the analysis of the three simpler compounds formed ic acid by analogous reactions shows that the quantity of ust such as might have been anticipated, so that there is on to doubt the accuracy of the exceptional cases in the mbers of the series.

ding to Berthelot, tristearin, tripalmitin, and triolein, cal with the stearin, palmitin, and olein of the natural they are produced by the combination of 3 atoms of ted fatty acids ($C_nH_nO_4$) with 1 atom of glycerin, the act ation being attended with the separation of 6 atoms of These combinations of glycerin with the acids may be either by heating the acid and the glycerin together for urs in closed vessels at an elevated temperature; or by e glycerin and fatty acid with hydrochloric, sulphuric, c, or tartaric acid, and exposing the mixture for many a temperature of 212°. A partial formation of these urs, even without the aid of the stronger acids, if the nd the fatty acid be kept in contact for several months inary temperature.

ese neutral compounds of the higher fatty acids with glycerin are insoluble in water, but are soluble to some extent in boiling alcohol, and are readily soluble in ether. If treated with concentrated acids they are decomposed and acidified in the same manner as the natural fats; and they are all saponifiable,—that is, they are decomposed like the natural fats, into a fatty acid and glycerin, when boiled with an alkali. It has been found that whether monacid, diacid, or triacid in composition, these fats are all neutral in their reactions, and moreover when decomposed, they all yield glycerin of the same composition and condition of hydration.

Glycerin indeed, as a triatomic alcohol, forms three classes of ethers, just as the tribasic phosphoric acid forms three classes of salts, the three classes of ethers being severally represented by monostearin, distearin and tristearin; the three bodies being represented by the following formulæ, in which glycerin is supposed to contain the triatomic radicle $(C_6H_5)'''$; whilst the three atoms of hydrogen are successively displaced by one, two, or three atoms of the radicle of stearic acid:—

$$\overbrace{\left.\begin{matrix}(C_6H_5)''' \\ H_3\end{matrix}\right\}O_6}^{\text{Glycerin.}} \quad ; \quad \overbrace{\left.\begin{matrix}(C_6\,H_5)''' \\ C_{36}H_{35}O_2 \\ H_2\end{matrix}\right\}O_6}^{\text{Monostearin.}} \quad ; \quad \overbrace{\left.\begin{matrix}(C_6\,H_5)''' \\ (C_{36}H_{35}O_2)_2 \\ H\end{matrix}\right\}O_6}^{\text{Distearin.}} \quad ; \quad \overbrace{\left.\begin{matrix}(C_6\,H_5)''' \\ (C_{36}H_{35}O_2)_3\end{matrix}\right\}O}^{\text{Tristearin.}}$$

This view will explain the possibility of displacing the hydrogen by different acids, as in aceto-chlorobromhydrin, and some other complicated ethers of glycerin which will be briefly alluded to.

Monostearin has the aspect of bees' wax; it fuses at 141°·8, and solidifies at 140°. It is prepared by heating equal parts of stearic acid and glycerin to 392°, for a couple of days in a sealed tube: the substance thus formed is freed from excess of stearic acid by digestion with slaked lime at a temperature of 212° for a quarter of an hour. The lime combines with the excess of stearic acid, but does not decompose the monostearin, which is afterwards separated from the lime soap by digesting the mixture in hot ether, from which the stearin crystallizes in stellate doubly refracting needles. *Distearin* may be prepared by heating to 212° for six days, equal parts of glycerin and stearic acid; it resembles the first compound in appearance, crystallizing in oblique doubly refracting plates, which fuse at 136°·4, and become solid at 131°. *Tristearin*, which is identical with natural stearin, may be obtained by digesting monostearin for three hours at a temperature of 518° with 15 or 20 times its weight of stearic acid: it is purified from the excess of stearic acid by lime and ether, as directed for monostearin. Valeric, butyric, and acetic acids have each, in like manner, been combined with glycerin in three proportions; but no compound could be obtained with formic acid. It is interesting to remark that even the compounds with acetic acid present the appearance of oily bodies, though many of the simpler glycerides, such as monobutyrin ($C_{14}H_{14}O_8$), chlorhydrin ($C_6H_7ClO_4$), and monacetin ($C_{10}H_{10}O_8$), are very soluble in water. It is not unlikely that triacetin is one of the components of cod-liver oil, since acetic acid is found amongst the products of the saponification of this oil.

(1070) Glycerin has also been similarly combined with other organic acids, such as the benzoic and the camphoric; as well as with hydrochloric, hydrobromic, and hydriodic acids. In addition to the monacid and diacid derivatives of glycerin, Berthelot and De Luca (*Ann. de Chimie*, III. lii. 433) have succeeded, by methods which we proceed to exemplify, in forming compounds of glycerin, each of which contains three different acids, thus exhibiting in glycerin the existence of a property parallel to that which has been long recognised in phosphoric acid; this acid having the power of forming salts which contain three different bases.

Chlorhydrin ($C_6H_7ClO_4$; *Boiling pt.* 440°) is obtained by saturating glycerin with hydrochloric acid gas, and maintaining the mixture at 212° for thirty-six hours: it is to be neutralized with carbonate of potash, and agitated with ether; the ethereal solution when evaporated leaves chlorhydrin as a neutral oil, with a cooling ethereal odour, and a sweetish, pungent taste. It is soluble in water and in ether, and may be distilled unchanged.

The formula of chlorhydrin only differs from that of tritylglycol by the substitution of an atom of chlorine for one of hydrogen; and Lourenço, by dissolving chlorhydrin in about its own bulk of water, and treating it with an amalgam of sodium, has succeeded in obtaining tritylglycol from it. By a reaction exactly analogous, the chlorhydrin of ordinary glycol has been converted into vinic alcohol:—

Chlorhydrin . . . $= C_6H_7ClO_4$; Tritylglycol $= C_6H_8O_4$;
Chlorhydrin of glycol $= C_4H_5ClO_2$; Alcohol . $= C_4H_6O_2$.

Dichlorhydrin ($C_6H_6Cl_2O_2$): *Sp. gr.* 1·37; *Boiling pt.* 352°.—This is a neutral oil which has a well-marked ethereal odour. It remains liquid at —30°. It burns with a white flame, bordered with green.

Trichlorhydrin ($C_6H_5Cl_3$; *Boiling pt.* 311°) may be obtained by acting upon the preceding compound with perchloride of phosphorus. It is a neutral liquid, insoluble in water.

Epichlorhydrin ($C_6H_5O_2Cl$); *Sp. gr.* betweeen 1·2 and 1·3.—This substance is a limpid oil which boils between 248° and 266°, emitting a vapour of an ethereal odour resembling that of hydrochloric ether. It *differs from chlorhydrin* by containing 2 atoms less of water. It is prepared by heating dichlorhydrin for seve hours in a sealed tube to 212°, with 12 or 15 parts of fu hydrochloric acid; after which it is neutralized with lime and di tilled. The mode in which these chlorinated compounds a formed is indicated in the Table at page 279.*

Epidichlorhydrin ($C_6H_4Cl_2$; *Boiling pt.* 248°) is formed in sma quantity during the preparation of trichlorhydrin; it assumes t form of a neutral, ethereal oil. It contains 2 atoms of water l than dichlorhydrin and 1 atom of hydrochloric acid less th trichlorhydrin.

All these chlorinated compounds when digested with moist ox of silver slowly part with their chlorine, and reproduce glycerin

Aceto-dichlorhydrin ($C_{10}H_8Cl_2O_4$; *Boiling pt.* 401°).—If a qu tity of pure glycerin be placed in a tubulated retort kept cool b immersion in water, and acetic oxychloride be added drop by d until it ceases to produce any action, a compound is form attended with violent extrication of heat. The product must distilled, washed first with water, then with a weak solution alkali, and after allowing it to stand upon a mixture of chlorid calcium and caustic potash in fragments, is redistilled. A neut limpid, colourless oil with an ethereal cooling odour is obtain whilst water and hydrochloric acid are separated, by the reac of hydrogen and oxygen derived from the glycerin upon oxychloride:—

$$\overbrace{C_{10}H_8Cl_2O_4}^{\text{Aceto-dichlorhydrin.}} = \overbrace{C_6H_8O_6}^{\text{Glycerin.}} + \overbrace{C_4H_4O_4}^{\text{Acetic acid.}} + 2\,HCl - 3\,H_2O_2.$$

A small quantity of *aceto-chlorhydrin* ($C_{10}H_9ClO_6$; *Boiling* 482°) is formed at the same time.

Aceto-chlorobromhydrin $C_{10}H_8ClBrO_4 = C_6H_8O_6 + C_4H_4O$ $HCl + HBr - 3\,H_2O_2$.—If a mixture of equivalent quantities acetic oxychloride and acetic oxybromide be made to act o glycerin in the manner just described, a compound will be form in which, by the elimination of 6 atoms of water, the ac hydrochloric and hydrobromic acids will have entered i combination with the glycerin, giving rise to a limpid, co less, ethereal liquid, insoluble in water, and boiling at ab 442°. Various other analogous compounds have been obtai but they are often difficult to purify, owing to their tendency become decomposed if distilled.

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* It is to be observed that in these compounds whenever chlorin halogen enters by displacement into the body, it is in a certain sense eq lent to HO_2; thus chlorhydrin = $C_6H_7ClO_4$, or glycerin in which H removed, whilst Cl has entered in its place.

We find, however, that sometimes several atoms of glycerin enter into combination with a single atom of an acid, whilst a variable number of atoms of water is eliminated. The following compounds for example, have been obtained :—

Hemibromhydrin	$C_{12}H_9BrO_4 = 2\,(C_6H_8O_6) + HBr - 4\,H_2O_2$.
Hexaglyceric bromhydrin	$C_{36}H_{27}BrO_{14} = 6\,(C_6H_8O_6) + HBr - 11\,H_2O_2$.
Iodhydrin . .	$C_{12}H_{11}IO_6 = 2\,(C_6H_8O_6) + HI - 3\,H_2O_2$.

Iodhydrin ($C_{12}H_{11}IO_6$) *Sp. gr.* 1·783.—When glycerin is saturated with hydriodic acid gas, and heated to 212° for forty hours, then treated with potash and with ether, it yields a golden yellow syrupy liquid, which dissolves one-fifth of its bulk of water, but is not itself soluble in water. The formation of this body is rather anomalous; $2\,C_6H_8O_6 + HI$ yielding $C_{12}H_{11}IO_6 + 3\,H_2O_2$. Iodhydrin has a sweet taste; it is combustible, and cannot be distilled without experiencing decomposition. When treated with an aqueous solution of potash it is slowly decomposed; iodide of potassium, and glycerin are formed, together with a volatile compound, which is soluble in ether, and which has a composition represented by $(C_6H_5O_3)_2$. This substance would correspond to the ether of glycerin. This supposed *glyceric ether* contains the elements of 2 atoms of glycerin, minus 6 atoms of water: $2\,C_6H_8O_6 = (C_6H_5O_3)_2 + 3\,H_2O_2$; and its formation from iodhydrin might be thus represented :—

$$2\,\overbrace{C_{12}H_{11}IO_6}^{\text{Iodhydrin.}} + 2\,(KO,HO) + H_2O_2 = 2\,\overbrace{C_6H_8O_6}^{\text{Glycerin.}} + \overbrace{(C_6H_5O_3)_2}^{\text{Glyceric ether.}} + 2\,KI.$$

Wurtz, however, did not succeed in procuring it.

Glycerin forms with hydrobromic acid compounds analogous to those which it yields with hydrochloric acid, such as *monobromhydrin* ($C_6H_7BrO_4$), *dibromhydrin* ($C_6H_6Br_2O_2$) and *tribromhydrin* ($C_6H_5Br_3$). When an alcoholic solution of dibromhydrin ($C_6H_6Br_2O_2$) is submitted to the action of gaseous ammonia, the hydrobromate of a new base, *glyceramine*, $C_6H_9NO_4$ (Berthelot and De Luca), is produced, whilst bromide of ammonium is formed.

Acid glycerides may be formed by causing glycerin to combine with a dibasic acid; thus we may obtain a monobasic glyceritartaric acid :—

$$\overbrace{C_{14}H_{12}O_{16}}^{\text{Glycerimono-tartaric acid.}} = \overbrace{C_6H_8O_6}^{\text{Glycerin.}} + \overbrace{C_8H_6O_{12}}^{\text{Tartaric acid.}} - H_2O_2.$$

Also a dibasic acid formed by a decomposition which may be th represented :—

$$\overbrace{C_{22}H_{16}O_{26}}^{\text{Glyceridi-tartaric acid.}} = \overbrace{C_6H_8O_6}^{\text{Glycerin.}} + 2\ \overbrace{C_8H_6O_{12}}^{\text{Tartaric acid.}} - 2\ H_2O_2\ ;$$

in addition to which an intermediate monobasic acid is known

$$\overbrace{C_{22}H_{14}O_{24}}^{\text{Epiglyceridi-tartaric acid.}} = \overbrace{C_6H_8O_6}^{\text{Glycerin.}} + 2\ \overbrace{C_8H_6O_{12}}^{\text{Tartaric acid.}} - 3\ H_2O_2.$$

Diethylin ($C_{14}H_{16}O_6$; *Sp. gr.* 0·92) is a limpid oil a pungent, ethereal odour; it boils at 376°, and does become solid at —40° ; it is scarcely soluble in water. This sing compound is obtained by acting upon a mixture of bromid ethyl, glycerin, and hydrate of potash ; the materials are encl in a sealed tube, and submitted for four days to a temperat of 212° :—

$$\overbrace{2\ C_4H_5Br}^{\text{Bromide of ethyl.}} + \overbrace{C_6H_8O_6}^{\text{Glycerin.}} + 2\ (KO,HO) = \overbrace{C_{14}H_{16}O_6}^{\text{Diethylin.}} + 2\ KBr + 2\ H_2O_2$$

or it may be regarded as the result of the combination of 2 al of alcohol and 1 of glycerin, attended with the separation of atoms of water, representing a double or mixed ether $\left.\begin{matrix}(C_6H_5)''' \\ H \\ (C_4H_5)_2\end{matrix}\right\}$

For the further prosecution of this subject the reader is refer to the papers of Berthelot in the *Annales de Chimie*, and to on the ethers of *glycide* by Reboul, *ib.* lx. 5.

(1071) *Acrolein, or Acrylic Aldehyd* ($C_6H_4O_2=C_6H_3O_2$, *Sp. gr. of vapour* 1·897.—When glycerin or any of its compo is submitted to the ordinary process of distillation, it underg decomposition; and amongst the products is a substance wh from its intensely irritating effects upon the mucous membran the eyes and organs of respiration, has received the name of *acrol* This substance is best obtained in a state of purity (Redtenbac *Liebig's Ann.* xlvii. 114), by distilling in a capacious retort mixture of glycerin with anhydrous phosphoric acid, or bisulphate of potash : the vapours must be condensed in a cup cooled receiver, which is luted on to the retort, and provided a tube opening into a chimney with a good draught.

The object of using anhydrous phosphoric acid in the distill is to effect the dehydration of the glycerin, since glycerin cont the elements of acrolein, and 4 equivalents of water.

$$\underbrace{C_6H_8O_6}_{\text{Glycerin.}} = \underbrace{C_6H_4O_2}_{\text{Acrolein.}} + 2\,H_2O_2.$$

The distilled liquid separates into two layers, the upper one isting of acrolein, and the lower one of an aqueous solution of same substance, mixed with a quantity of acrylic acid. This illate must be digested with finely powdered litharge which enters combination with the acid, and then rectified by the heat of a er-bath: the acrolein thus obtained must be submitted to a second ification from chloride of calcium, after which it is nearly free impurity. All these operations must be carried on in vessels d with carbonic acid, for the purpose of excluding atmospheric gen, because acrolein becomes rapidly oxidized when exposed to air.

Acrolein is a limpid, transparent, colourless liquid, lighter than er, and possessed of a high refracting power. It has a burning e, and emits a vapour which is intolerably irritating; the boiling t of the liquid is about 125°. It burns with a clear luminous e. Acrolein when pure is neutral to test paper; but, like ary aldehyd, it rapidly becomes acid by the absorption of en from the air; a mixture of acrylic, acetic, and formic being produced. In fact, it contains 2 atoms of oxygen less acrylic acid, to which it stands in the same relation as ordi- y aldehyd does to acetic acid. Acrolein is freely soluble in r, but requires 40 parts of water for solution. It cannot long be rved without change, even in sealed tubes; but becomes con- rted into a white, flocculent, and probably isomeric substance, med *disacryl;* this compound is insoluble in water, acids, alkalies, and bisulphide of carbon. Sometimes the acrolein becomes formed into a resinoid body, which melts at 212°, and forms ittle, transparent mass on cooling; this substance, though inso- le in water, is soluble in alcohol, in ether, and in alkaline solutions.

The reactions of acrolein with the alkalies, further show its ilarity to aldehyd:—when mixed with a solution of potash or of it is rapidly acted upon; its irritating odour disappears and is eded by one of cinnamon, whilst a brown resinous substance is rmed. The ethereal solution of acrolein when mixed with ammo- yields a white amorphous body, destitute of odour. When with nitrate of silver it gives a white curdy precipitate, which ced to metallic silver on boiling, though without coating the ith the reduced metal; acrylate of silver remains in solu- Oxide of silver rapidly oxidizes acrolein, with great evolu- eat, and converts it into acrylic acid (1125); the acid is indeed easily prepared by this means from the crude liquid obtained by the destructive distillation of the fixed oils.

Hofmann and Cahours have succeeded in discovering the *allylic alcohol* (C_6H_5O, HO), a compound which stands in the same relation to acrolein that ethylic alcohol does to ordinary aldehyd: many of the derivatives of this alcohol have been long known as compounds of *allyl* (C_6H_5).

§ III. OTHER POLYATOMIC ALCOHOLS.

No triatomic alcohol except glycerin has yet been definitely proved to exist; but it is probable that mannite, and its congeners pinite, dulcite and quercite, as well as glucose and some other sugars, are polyatomic alcohols of still greater complexity than glycerin.

(1072) *Compounds of Mannite with the Acids, analogous to Fats.*—The investigations of Berthelot upon the combinations of saccharine bodies with the acids have disclosed the existence of a series of compounds presenting a remarkable analogy with the fats. (*Ann. de Chimie*, III. xlvii. 297). When mannite is heated for some hours with the hydrated acids in sealed tubes under pressure, it gives rise to a series of compounds which run exactly parallel with those obtained by treating glycerin in a similar manner. If stearic acid be thus heated with mannite it forms two compounds, viz., *distearo-mannite* and *tristearo-mannite*, which may be represented as formed thus:—

$$\overbrace{C_{12}H_{14}O_{12}}^{\text{Mannite.}} + 4\ \overbrace{C_{36}H_{36}O_4}^{\text{Stearic acid.}} = \overbrace{C_{156}H_{152}O_{22}}^{\text{Distearo-mannite.}} + 3\ H_2O_2;$$

$$C_{12}H_{14}O_{12} + 6\ C_{36}H_{36}O_4 = \overbrace{C_{228}H_{216}O_{22}}^{\text{Tristearo-mannite.}} + 7\ H_2O_2.$$

These substances can scarcely be distinguished from distearin and tristearin, which are the corresponding compounds of glycerin; they are solid crystalline fats, of about the same degree of fusibility as the stearins. They admit of being saponified in the same manner as the true fats; and when decomposed by bases they yield stearic acid, and a solution from which the sweet syrupy compound, mannitane (945), is obtained. This solution so greatly resembles that of glycerin in appearance and properties, that Berthelot thinks it is by no means improbable that some of the natural fats which are at present supposed to be compounds of glycerin, may turn out to be derivatives of mannite. Compounds of mannite similar to those which it forms with stearic acid, have been obtained by heating it with palmitic, butyric, acetic, benzoic, and other acids. Its compound with acetic acid, *aceto-mannite*, ($C_{20}H_{16}O_{14}=C_{12}H_{14}O_{12}+2\,C_4H_4O_4-3\,H_2O_2$) is a viscid, intensely bitter liquid, which emits, when warmed, a peculiar odour like that possessed by many of the umbelliferous plants. With hydrochloric acid, mannite yields a white, neutral, well-crystallized body, *chlorhydromannite* ($C_{12}H_{10}Cl_2O_6$), which has a bitter aromatic taste: it is very soluble in ether, and may be volatilized without residue. The fat-like derivatives of mannite are neutral bodies. Those which are produced from two equivalents of acid may be supposed to be formed by the union of 1 atom of *mannitane* and 2 atoms of the normal hydrate of the acid, attended with the separation of 4 atoms of water; whilst those containing 6 equivalents of acid are formed from one of mannitane and 6 of the normal acid, with the separation of 12 atoms of water. Mannitane rather than mannite therefore is the analogue of glycerin.

Mannite also forms compounds with the polybasic acids, such as the sulphuric, the tartaric, and the phosphoric acids; these compounds have an acid character, and are analogous to the sulphoglyceric and phosphoglyceric acids (1068).

(1073) *Action of Polybasic Acids upon the Sugars.*—Berthelot has shown that most of the saccharine bodies enter into combination with various polybasic acids, forming with them colligated acids analogous in composition to tannic acid (1157). If for example, powdered tartaric acid be intimately mixed with an equal weight of sucrose, glucose, lactose, sorbin, pinite, quercite, mannite, or erythro-mannite, and be exposed in an open vessel for a day or two to a temperature of about 248°, the acid enters into combination with the saccharine body more or less perfectly. In order to isolate the new body, the mass is allowed to cool, and is afterwards triturated with water and carbonate of lime. The excess of tartaric acid is thus removed in the form of tartrate of lime, which is insoluble, whilst a salt of lime with the new colligated acid remains in solution, mixed with the excess of uncombined saccharine matter. On the addition to the filtrate of twice its bulk of alcohol, the lime salt is precipitated, and may be purified by washing with alcohol of sp. gr. 0·920. The purification is completed by redissolving the salt in water and repeating the precipitation with alcohol, once or twice more. If the salt thus obtained be treated with an equivalent proportion of oxalic acid, the new acid is set at liberty.

During the formation of these colligated acids the saccharine body loses the elements of water in the act of combining with the polybasic acid, whilst the basic power of the acid is dimin in the analogous case of the combination of sulphu with the elements of alcohol (985) in the preparation o ethylic acid.

The following equations will serve to elucidate the con of some of these sucro-acids :—

1. *Sucro-tartaric acid,* dibasic :—

$$4\,\overbrace{(2\,HO,C_8H_4O_{10})}^{\text{Tartaric acid.}}+2\,\overbrace{C_{12}H_{11}O_{11}}^{\text{Sucrose.}}=2\,(\overbrace{2\,HO,C_{28}H_{13}O_{30}}^{\text{Sucro-tartaric acid.}})+3\,H$$

2. *Gluco-tartaric acid,* dibasic :—

$$2\,\overbrace{(2\,HO,C_8H_4O_{10})}^{\text{Tartaric acid.}}+\overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}=(\overbrace{2\,HO,C_{28}H_{18}O_{28}}^{\text{Gluco-tartaric acid.}})+4\,H_2O$$

3. *Lacto-tartaric acid,* dibasic :—

$$4\,\overbrace{(2\,HO,C_8H_4O_{10})}^{\text{Tartaric acid.}}+3\,\overbrace{C_{12}H_{12}O_{12}}^{\text{Lactose.}}=2\,(\overbrace{2\,HO,C_{34}H_{24}O_{36}}^{\text{Lacto-tartaric acid.}})+4\,H$$

A tribasic lacto-tartaric acid was obtained on one occas tribasic *mannitartaric* and tribasic *gluco-citric* acid app wise to exist.

(1074) *Saccharides* and *Glucosides.*—In pursuing t searches Berthelot (*Ann. de Chimie,* III. lx. 93) has suc forming a variety of neutral compounds by the action upon glucose, and on other varieties of sugar. The form the splitting up of these saccharides are effected under c similar to those which are applicable to the neutral fat indeed the chemical and physical properties of these tw of complex principles are very similar. The saccharides ever much more alterable and are more difficult to pro the neutral fats, or even than the still more closely allied compounds of this nature.

A stearic glucose for example may be formed by h 250° for 50 or 60 hours a mixture of anhydrous grape cane sugar, or of trehalose with stearic acid :—

$$\overbrace{C_{12}H_{12}O_{12}}^{\text{Glucose.}}+2\,\overbrace{C_{36}H_{36}O_4}^{\text{Stearic acid.}}-3\,H_2O_2=\overbrace{C_{84}H_{[illegible]}O_{[illegible]}}^{\text{Stearic glucose.}}$$

It is a colourless, waxy, fusible solid, soluble in eth absolute alcohol, but insoluble in water.

By analogous methods benzoic, butyric, and [illegible] have been obtained as neutral oils :—

$$\overbrace{C_{12}H_{12}O_{12}}^{\text{Glucose.}}+2\,\overbrace{C_{14}H_6O_4}^{\text{Benzoic acid.}}-3\,H_2O_2=\overbrace{C_{40}H_{[illegible]}O_{[illegible]}}^{\text{Benzoic [illegible]}}$$

$$C_{12}H_{12}O_{12} + 2\overbrace{C_8H_8O_4}^{\text{Butyric acid.}} - 3\,H_2O_2 = \overbrace{C_{28}H_{22}O_{14}}^{\text{Butyric glucose.}};$$

$$C_{12}H_{12}O_{12} + 6\overbrace{C_4H_4O_4}^{\text{Acetic acid.}} - 7\,H_2O_2 = \overbrace{C_{33}H_{22}O_{22}}^{\text{Acetic glucose.}}.$$

sulphuric acid decomposes these compounds when heated
em, the elements of water being assimilated, whilst the
acid and fermentable sugar are reproduced. If heated
mixture of alcohol and hydrochloric acid, fermentable
liberated, whilst the ether of the organic acid,—benzoic,
or acetic ether is produced. They all reduce the
tartrate of copper and potash.

only do the sugars thus unite with the acids, but like the
ic alcohols they may also combine with the radicles of
cohols, or with the radicles of both acids and alcohols.
mpounds are analogous to the glycerides. *Ethyl-glucose*
ple is obtained by heating to 212° for several days a mix-
ane sugar, bromide of ethyl, and hydrate of potash. The
luct is dissolved by means of ether, and remains after the
evaporated *in vacuo* :—

$$\overbrace{H_{12}O_{12}}^{\text{cose.}} + 2\overbrace{C_4H_5Br}^{\text{Bromide ethyl.}} + 2\,(KO,HO) = \overbrace{C_{20}H_{18}O_{10}}^{\text{Ethyl-glucose.}} + 2\,KBr + 3\,H_2O_2.$$

red oil which is not volatilizable is thus obtained. It is of
taste and faint agreeable odour resembling that of old
Many substances resembling this compound occur na-
such for instance as salicin, phloridzin, arbutin, and

will be observed that the glucosides are formed from a
y of glucose, which yields 2 atoms more of water than
have been expected from the analogous reactions with
; the body which corresponds to the alcohol having the
ition $C_{12}H_{10}O_{10}$—this body however has not been isolated—
rthelot suggests for it the name of *glucosane*, to indicate
logy with mannitane.

cose yields, by careful heating, a compound $C_{12}H_{10}O_{10}$,
Gélis terms *saccharide* (p. 78).

rther researches upon the derivatives of sugar are, however,
to clear up several points which are still but little under-

CHAPTER V.

PRODUCTS OF THE OXIDATION OF THE ALCOHOLS—A

§ I. The Aldehyds and Acetones.

(*a*) *The Aldehyds.*

(1075) Allusion has been already made on several to the important series of acids which are produced by t tion of the alcohols, but a series of compounds may be which are less highly oxidized than the acids, which sta intermediate position between the alcohols and the acid have received the name of aldehyds. Many of the pro these bodies are remarkable.

It has already been mentioned that when alcohol i with free access of air, the sole products are carbonic water. If, however, the combustion be effected at a lo perature, and with a limited supply of air, numerous ot pounds are formed, and the vapours emitted have a irritating effect on the eyes and nose, due principally to duction of a remarkable body, named *aldehyd.* The a fact, is imperfectly burned; in each molecule of alcoho of hydrogen are converted into water by union with 2 e of oxygen from the air, and aldehyd (*al*cohol *dehydr*og obtained:—

$$2\,\overbrace{C_4H_6O_2}^{\text{Alcohol.}}+O_4=2\,\overbrace{C_4H_4O_2}^{\text{Aldehyd.}}+2\,H_2O_2.$$

Similar compounds are furnished by the imperfect com the other alcohols. The following are the principal bod class which have been examined:—

Compounds.	Formula.	Specific Gravity.	
		Liquid.	Gaseous.
Formic aldehyd? . .	$C_2H_2O_2$		
Acetic aldehyd . . .	$C_4H_4O_2$	0·79	1·532
Propionic aldehyd . .	$C_6H_6O_2$	0·79	2·169
Butyric aldehyd . . .	$C_8H_8O_2$	0·80	
Valeric aldehyd . . .	$C_{10}H_{10}O_2$	0·82	2·96
Caproic aldehyd . . .	$C_{12}H_{12}O_2$		
Œnanthylic aldehyd .	$C_{14}H_{14}O_2$	0·827	4·178
Caprylic aldehyd . .	$C_{16}H_{16}O_2$	0·818	
Capric aldehyd . . .	$C_{20}H_{20}O_2$		
Euodic aldehyd . . .	$C_{22}H_{22}O_2$	0·849	5·87
Lauric aldehyd . . .	$C_{24}H_{24}O_2$		6·182

he aldehyds are characterized by their remarkable tendency nbine with oxygen, in consequence of which they absorb it re exposure to the air, and become acid. Each molecule of yd absorbs 2 atoms of oxygen, and is converted into the ponding acid; for example:—

$$\overbrace{2\ C_4H_4O_2}^{\text{Acetic aldehyd.}}+O_4 = 2\ \overbrace{(HO,C_4H_3O_3)}^{\text{Acetic acid.}};$$

$$\overbrace{2\ C_8H_8O_2}^{\text{Butyric aldehyd.}}+O_4 = 2\ \overbrace{(HO,C_8H_7O_3)}^{\text{Butyric acid.}}.$$

ost of the aldehyds combine with ammonia, and form with it lline compounds which are insoluble in ether. When mixed a solution of potash, they form with the alkali a brown us mass. Many of them when heated with a solution of of silver, to which a small quantity of ammonia has been , decompose the salt of silver, and reduce the metal in the of a mirror-like coating upon the inner surface of the vessel ich they are heated. Another remarkable property of the yds is their power of forming with the bisulphite of potash soda crystalline compounds of stable character and sparing lity. These compounds contain the elements of one atom ulphite of the alkali, and one of the aldehyd, with or without of crystallization, having the general formula, (HO,KO,S_2O_4 $H_{2n}O_2+x$Aq). Many essential oils, such as those of bitter ds, cinnamon, cummin, and spiræa, form similar compounds. essences are probably the aldehyds of a different class of ols (973).

The aldehyds are polymeric with the ethers of the acid in the s to which they belong, but they yield vapours of but half the ty of that of the corresponding compound ether:—Thus c aldehyd is polymeric with acetic ether; $2\ C_4H_4O_2=C_8H_8O_4$ $H_5O,C_4H_3O_3$; and valeric aldehyd is polymeric with valerate myl; $2\ C_{10}H_{10}O_2=C_{20}H_{20}O_4=C_{10}H_{11}O,C_{10}H_9O_3$.

The theoretical composition of the aldehyds has been variously sented. Liebig proposed to regard acetic aldehyd as $H_3)O,HO$, or as the hydrated oxide of a peculiar radicle C_4H_3, ed *acetyl*; and a similar view would of course be applicable to aldehyds since discovered: they may also be regarded as comds in some measure analogous to hydrogen itself, acetic yd being then represented by the formula $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}$, in dance with the hydrogen *type* $\left.\begin{matrix}H\\H\end{matrix}\right\}$. These views will be discussed more fully when the properties of acetic aldehyd considered.

The aldehyds are unstable compounds, several of them pa into bodies which are isomeric with them, but which possess perties entirely different from the true and rapidly oxidi aldehyds.

(1076) FORMIC ALDEHYD has not hitherto been satisfact isolated, but *methylal*, a body homologous with acetal, is conta amongst the products of the gradual oxidation of wood spir means of peroxide of manganese and sulphuric acid.

(1077) 2. ALDEHYD, *Acetic aldehyd* ($C_4H_4O_2$) : *Sp. gr. of l at* 32°, 0·8009; *of vapour* 1·532; *Boiling pt.* 67°·8 (Kop Acetic aldehyd was the earliest discovered member of the g of aldehyds, and owing to its connexion with the process of a fication it is by far the most important of them.

Preparation.—Aldehyd may be obtained by the gradual o tion of alcohol in various ways: thus it is formed whe vapour of alcohol mixed with air is transmitted through a p lain tube heated to low redness, or when alcohol is acted by dilute nitric or chromic acid: owing to the action of acid upon the elements of alcohol, it is produced during the paration of the fulminates of silver and of mercury, and always present in nitrous ether: it may also be procured b dry distillation of lactic acid, or of lactate of copper. An remarkable mode in which aldehyd may be obtained has pointed out by Natanson: he finds that when chloride of dieth nium (1197) is mixed with nitrite of silver and a little sulp acid, a copious evolution of nitrogen occurs, and aldehyd is for abundantly;—

$$\overbrace{C_4H_4)_2''H_4N_2Cl_2}^{\text{Chloride of diethylenium.}} + 2\,(AgO,NO_3) = 2\,\overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\,N_2 + 2\,H_2O_2 + 2\,Ag$$

Diethylenium is itself derived from Dutch liquid by the act ammonia upon it; whence it would appear that a close rela ship exists between olefiant gas and aldehyd.

None of these reactions are employed for the preparati aldehyd, since there are more convenient methods. One of consists in placing 3 parts of bichromate of potash in a retort, allowing a mixture of 4 parts of sulphuric acid diluted w times its volume of water to flow into the retort, containing of alcohol, cooled by immersion in a freezing mixture; distill commences without the aid of heat; the vapours must be densed in a proper refrigeratory.

Aldehyd is however usually procured by Liebig's method of distilling in a capacious retort, a mixture of 6 parts of sulphuric acid, 4 of alcohol (sp. gr. 0·850), 4 of water, and 6 of finely powdered black oxide of manganese. In this process the oxide of manganese is decomposed, sulphate of protoxide of manganese is formed, whilst the second atom of the oxygen of the binoxide of manganese combines with the hydrogen of part of the alcohol, and aldehyd is formed and passes over. The product being very volatile must be condensed in vessels cooled with ice, and the process must be stopped when the distillate becomes acid. Since, however, it is in a very dilute and impure condition, it is to be rectified from an equal weight of chloride of calcium, in order to free it from alcohol and water. This operation is repeated twice, or even three times. The distilled liquid still retains alcohol, besides a small quantity of acetic ether, and a liquid termed acetal (1079). For the purpose of obtaining it free from these impurities it is mingled with twice its bulk of anhydrous ether, and saturated with dry ammoniacal gas, while the liquid is artificially cooled: prismatic needles of snowy whiteness are thus formed; these crystals consist of a compound of aldehyd with ammonia ($H_3N,C_4H_4O_2$) which is insoluble in ether, though very soluble in water; they may be dried in the open air; they fuse at a heat a little below 212°, and at 212° may be sublimed unchanged. If heated in the open air they take fire, and burn with flame. After a time, even when kept in closed vessels, the crystals become brown, and emit an odour like that of burned feathers. To obtain pure aldehyd from them, 2 parts of the crystals dissolved in 2 of water, are distilled with 3 of oil of vitriol diluted with 4 parts of water; the product is received in vessels surrounded with ice, and is finally rectified from chloride of calcium.

Properties.—Aldehyd is a volatile inflammable liquid, with a peculiar pungent irritating odour, which has a faint resemblance to that of apples. It may be mixed in all proportions with alcohol, ether, and water. It has no acid reaction upon litmus paper, but it can scarcely be exposed to the air without absorbing oxygen, and it then forms an acid compound. Aldehyd yields with ammonia the peculiar crystalline body already described, but when similarly treated with potash it gives a brown resinous mass: this is one of its most characteristic reactions. Another striking one is its power of reducing the oxide of silver, and of yielding, when boiled with solutions of the salts of this metal, a mirror-like coating of silver upon the sides of the tube in which the experiment is made: the solution should be rendered feebly alkaline

by the addition of a few drops of a weak solution of amm
In this experiment a portion of the aldehyd is converted
an acid, at the expense of the oxygen derived from a porti
the oxide of silver which is thus reduced to the metallic state
the newly formed acid enters into combination with a porti
the undecomposed oxide of silver.

Chlorine displaces a portion of the hydrogen of the ald
converting it into chloral (1021);

$$\overbrace{C_4H_4O_2}^{\text{Aldehyd.}}+3\,Cl_2=\overbrace{C_4Cl_3HO_2}^{\text{Chloral.}}+3\,HCl.$$

Aldehyd, when transmitted over a mixture of lime and hydr
potash in a heated tube, first becomes brown, and is then d
posed with disengagement of hydrogen, leaving a white
composed of acetate of potash :—

$$\overbrace{C_4H_4O_2}^{\text{Aldehyd.}}+KO,HO=\overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}}+H_2.$$

Potassium when placed in contact with aldehyd disengages
gen, and forms a soluble compound ($C_4H_3O_2K$) possessed
alkaline reaction, which absorbs oxygen readily. This com
contains the elements of aldehyd, in which one atom of pot
has displaced one of hydrogen.

According to Lieben (*Liebig's Annal.* cvi. 336) if aldeh
saturated with dry hydrochloric acid, while kept cold by imm
in a freezing mixture, the liquid separates into two laye
lower one being an aqueous solution of hydrochloric acid a
upper one consisting of $C_8H_8Cl_2O_2$ (*Sp. gr. of vapour* 5·08;
pt. 241°). He terms this liquid *oxychloride of ethyliden.*
decomposed by hot water into aldehyd and hydrochloric aci

Aldehyd if heated with acetic anhydride to 360° in a
tube unites with it, forming a colourless liquid ($C_4H_4O_2$,C
isomeric with binacetate of glycol; it boils at 336°. Simila
pounds may be formed with benzoic and succinic anhy
If aldehyd be heated with chloride of acetyl, in sealed tub
two bodies unite, forming a liquid ($C_8H_7ClO_4$) which boils b
248° and 255°.

Aldehyd, even when preserved in sealed tubes, has been
to undergo a remarkable spontaneous conversion into tw
substances, each isomeric with it; one of these is a solid cry
body, *metaldehyd*, which may be sublimed at 248°, before
going fusion: the other retains the liquid form and is termed
hyd; the latter may be mixed with water, alcohol, and ether, in

portions; it boils at 201°, and freezes at 35°·6. The density of its vapour according to Fehling is 4·5157, which is three times that of aldehyd; elaldehyd appears therefore to have been formed by the condensation of the elements of three molecules of aldehyd into one. A third isomeric body termed *paraldehyd*, is a liquid which solidifies at 50°, and boils at 257°; it is formed when aldehyd diluted with an equal bulk of water is exposed with a trace of sulphuric or nitric acid to a cold of 32°; crystals of metaldehyd are deposited, and paraldehyd remains in the liquid; the sp. gr. of its vapour is 4·583; its molecular volume coinciding with that of elaldehyd, with which indeed it is by some chemists believed to be identical. A similar change of aldehyd into paraldehyd occurs when the aldehyd is digested for some hours at 212° in a sealed tube with iodide of ethyl or with cyanogen (Lieben).

Aldehyd absorbs sulphurous acid with avidity. This appears to be a simple case of solution, as the sulphurous acid may be entirely displaced by a current of carbonic acid gas: but the aldehyd gradually passes into paraldehyd, which if heated gently with dilute sulphuric acid is converted into ordinary aldehyd.

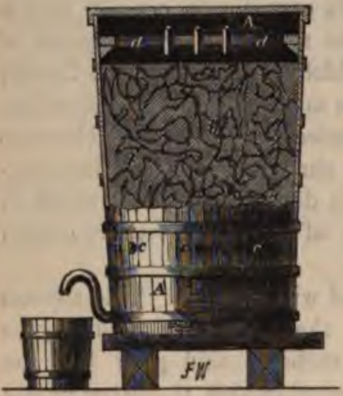
When aldehyd is digested in a sealed tube for some hours at 212° with a saturated solution of formiate of soda, or of tartrate of soda and potash, it gradually loses the elements of water, and a new compound is formed ($C_8H_6O_2$):—

$$2\,C_4H_4O_2 - H_2O_2 = C_8H_6O_2.$$

The nature of aldehyd and its isomerides is at present only imperfectly understood; but it has recently attracted much attention owing to its close relation to glycol and its derivatives, as well as to the polyatomic bases of the ethylene series (1196).

(1078) *Preparation of acetic acid.*—The principal interest, however, with which aldehyd is invested, arises from the facility with which it absorbs oxygen, and its consequent connexion with the process of acetification. When alcohol is exposed to the united influence of atmospheric air and finely divided platinum, partial oxidation occurs, and aldehyd is produced in abundance: owing to the readiness with which aldehyd absorbs oxygen, an attempt was made to carry the oxidation a step further, and thus to prepare acetic acid on a large scale by this method. The use of platinum, however, is now abandoned, but the manufacture of vinegar upon this principle is still extensively followed. In Germany, and in other countries where the legislature imposes no duty upon alcohol, dilute spirit mixed with a small quantity of infusion of malt is the ordinary material employed in the manufacture of vinegar. The mode of procedure is the following :—Large vats, of the form shown at A, A, fig. 363, provided with a loosely fitting lid, are filled with deal or beech shavings, first dried, and then soaked in strong vinegar ; these shavings rest upon a perforated shelf which is supported just above the level of the lower apertures, *c*, *c*. Near the top of these vats is a shelf *d*, *d*, perforated with a multitude of minute holes, through each of which passes a piece of packthread, knotted at its upper end to prevent it from falling through ; this arrangement being intended to allow the spirit of wine to be slowly and equably distributed over the shavings. Through this shelf a few glass tubes project to allow free egress to the spent air, and at about $\frac{2}{3}$rds of the depth of the cask are a row of apertures *c*, *c*, to admit air. A mixture consisting of 1 part of alcohol, sp. gr. 0·850, of 6 parts of water, and $\frac{1}{1000}$th of honey, yeast, or wort, is then allowed to trickle slowly through the shavings, whilst the temperature is raised to about 80° F.

Fig. 363.



Pure diluted alcohol does not absorb oxygen when exposed to the atmosphere ; to induce its oxidation it requires the presence of some vegetable matter which is itself prone to absorb oxygen, and it is for this reason that honey or sweet wort is added. Liebig supposes that these bodies act much in the same way as yeast does, during its development and change, in disturbing the chemical equilibrium of the atoms of sugar in causing it to ferment. The acetification does not proceed rapidly until the process has been in operation for some days. By degrees a peculiar kind of fungus or slimy vegetable mould is formed upon the shavings, and which is known under the name of *mother of vinegar* ; this substance acts somewhat in the manner of a ferment, and accelerates the oxidation, probably owing to its own tendency to combine with oxygen. It is remarkable that the presence of a very minute quantity of any empyreumatic or tarry matter is sufficient entirely to put a stop to the transformation. As the operation proceeds, the heat rises to about 100° or 105° ; at which point it remains stationary.

he alcohol has been made to pass through the vat four or es, its conversion into vinegar is usually complete. Well- charcoal purified from saline matters by hydrochloric acid, en thoroughly washed, may be substituted for the shavings od effect. In this operation a large surface is exposed to aldehyd is formed, and it immediately absorbs oxygen from osphere, being thus at once converted into common vinegar c acid :—

$$2\,\overbrace{C_4H_6O_2}^{\text{Alcohol.}}+O_4 = 2\,\overbrace{C_4H_4O_2}^{\text{Aldehyd.}}+2\,H_2O_2;\ \text{and}$$

$$2\,\overbrace{C_4H_4O_2}^{\text{Aldehyd.}}+O_4 = 2\,(\overbrace{HO,C_4H_3O_3}^{\text{Acetic acid.}}).$$

he supply of air be insufficient, a large quantity of alcohol d, owing to the formation of aldehyd, which from its great y, passes off in vapour before it has become oxidized and d into acetic acid.

erent views have been taken of the nature of aldehyd. Gerhardt is now generally adopted; he considered that le of acetic acid contains oxygen, representing this radicle O_2, and he supposed that the other acids of the same ll contain homologous oxidized radicles; the radicle of cid, for instance, being C_2HO_2, that of butyric acid being and so on. The aldehyds were regarded by him as of these radicles with a tendency to become oxidized: hydrogen and the assumed radicle of the acid becoming simultaneously. These relations may be thus indicated :—

Radicle.		Aldehyd.	Hydrated acid.
ormic . .	$C_2\,H\,O_2$	$C_2\,H\,O_2.H$	$HO,C_2\,H\,O_2.O$
cetic . . .	$C_4\,H_3O_2$	$C_4\,H_3O_2.H$	$HO,C_4\,H_3O_2,O$
tyric . .	$C_8\,H_7O_2$	$C_8\,H_7O_2.H$	$HO,C_8\,H_7O_2,O$
alerie . .	$C_{10}H_9O_2$	$C_{10}H_9O_2.H$	$HO,C_{10}H_9O_2,O$

siderable probability is given to this view by the existence compounds in which the two atoms of oxygen assumed to the radicle are preserved in the compounds derived from erhardt does not admit the existence of acetous acid H_3O_2), or of bodies homologous with it.

tendency of aldehyd to rapid oxidation affords an expla- f the fact that platinum black always furnishes an acid pro-

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dized radicles of the aldehyds and of acids, appear to be iso- , so far as any radicles are truly isolable. Freund (*Liebig's* duct by its reaction on alcohol. Aldehyd is first formed, but it immediately undergoes partial oxidation, by which it is converted into a mixture consisting chiefly of acetal and acetic acid. By a process somewhat similar, weak fermented, but not distilled liquors frequently become sour when exposed to the air in warm weather,—a change which forms the basis of the usual method of preparing white wine and malt vinegars; the mucilaginous and albuminous matters present in the wort or beer absorb oxygen, and induce a similar process of oxidation in the alcohol, in consequence of which acetic acid is formed. The more completely fermentation has taken place, the less likely is vinegar to be formed; since, during the fermentation, the azotised and other matters necessary to further the oxidation of the alcoholic portion are gradually destroyed. If much albuminous matter remain in solution in the vinegar after it is formed, the acid is itself liable to undergo a further change: a peculiar mould or fungus appears upon the surface of the liquid, and the acid is slowly decomposed; the cellulin or ligneous tissue of the fungus being formed at the expense of the constituents of the acetic acid:—

$$9\,\overbrace{(HO,C_4H_3O_3)}^{\text{Acetic acid.}} = \overbrace{C_{36}H_{30}O_{30}}^{\text{Cellulin.}} + 3\ H_2O_2.$$

The formation of aldehyd appears always to precede the production of vinegar, just as the transformation of cane into grape sugar precedes the vinous fermentation. Acetification, however, is not a true process of fermentation; it is rather one of gradual oxidation, and differs from fermentation in the important fact that the absorption of oxygen is necessary during the whole course of the operation: 1 part of alcohol requiring more than $\frac{2}{3}$rds of its weight of oxygen for acetification; and if the supply of oxygen be arrested, the further production of acid is immediately stopped.

(1079) *Acetal* ($C_{12}H_{14}O_4 = 2\ C_4H_5O,C_4H_4O_2$) *Sp. gr. of liquid* 0·821; *of vapour* 4·24; *Boiling pt.* 221°.—This compound was discovered by Döbereiner among the products furnished by the slow oxidation of alcohol under the influence of finely divided platinum.

Annal. cxviii. 33) by acting upon butyric oxychloride with an amalgam of sodium, has succeeded in obtaining butyryl:—

$$2\,\overbrace{\left(\begin{matrix}C_8H_7O_2\\ Cl\end{matrix}\right\}}^{\text{Butyric oxychloride.}} + \left.\begin{matrix}Na\\ Na\end{matrix}\right\} = \overbrace{\left.\begin{matrix}C_8H_7O_2\\ C_8H_7O_2\end{matrix}\right\}}^{\text{Butyryl.}} + 2\left.\begin{matrix}Na\\ Cl\end{matrix}\right\}.$$

When distilled with hydrate of potash, butyryl yields butyrate of potash and a liquid of an agreeable fruity odour, which boils between 347° and 365°, and has the composition of butyrone ($C_{14}H_{14}O_2$).

r of watch glasses containing platinum black (823) are a jar, into the lower part of which a few ounces of alcohol n introduced: the jar is covered with a glass plate, and few days in a temperature of about 70°, taking care to e air in the jar from time to time. The alcohol rises in nd undergoes slow oxidation, the liquid becomes condensed sides of the jar, and the products collect at the bottom. d liquid thus obtained consists of a mixture of alcohol, acetic ether, and acetal. It is first rectified from car- potash; and on adding chloride of calcium to the distillate s any of the salt is dissolved, a layer of acetal is separated, to the surface: this is removed by means of a pipette, h the cautious addition of water to the solution of chloride n causes the separation of an additional quantity of the id. It is purified by rectifying it from chloride of cal- Vurtz obtains acetal abundantly from the crude distillate in the preparation of aldehyd (1077). The aldehyd is f by distillation, and passes over with the more volatile whilst the acetal is separated from the portion which distils 176° and 200°, by agitating it with potash to remove yd and compound ethers, and then rectifying from of calcium, as above directed. Acetal forms a colourless an agreeable characteristic odour, and a flavour resem- of hazel nuts. It is soluble in about 6 parts of water, ubility diminishes as the temperature rises: it is soluble portions in alcohol and ether. Aqueous solutions of the f excluded from the air, do not decompose acetal. (Stas. *Chimie*, III. xix. 151.) Oxidizing agents transform it aldehyd, and then into acetic acid. Acetal may be as a combination of aldehyd with ether; 3 molecules of ncurring to the production of 1 molecule of acetal:—

$$\overbrace{6\,C_4H_6O_2}^{\text{Alcohol.}} + O_4 = \overbrace{2\,(2\,C_4H_5O,C_4H_4O_2)}^{\text{Acetal.}} + 4\,H_2O_2.$$

z, however, views it as glycol in which 2 atoms of hydro- isplaced by 2 of ethyl; and by distilling wood spirit with manganese and sulphuric acid he has obtained a corre- compound in which 2 equivalents of methyl have taken of the 2 of hydrogen in glycol. This is a liquid which boils 185°, of sp. gr. 0·853, with a vapour density of 3·475.

) 3. *Propionic Aldehyd* ($C_6H_6O_2$): *Sp. gr. of liquid* 0·79; f 2·169.—The aldehyds which still remain to be noticed, aratively unimportant.

Propionic aldehyd was found by Guckelberger amongst t products furnished by distilling albuminous substances with a m ture of sulphuric acid and peroxide of manganese (Liebig's *Annal* lxiv. 42). It passes over mixed with acetic and butyric aldehy as well as with the oil of bitter almonds (hydride of benzoy Propionic aldehyd is a limpid liquid of an ethereal odour; it soluble in water, alcohol, and ether, in all proportions. It bo between 131° and 149°, and becomes slowly acid when exposed the air, yielding propionic acid.

(1081) 4. *Butyric Aldehyd* ($C_8H_8O_2$; *Sp. gr. of liquid* 0·8 obtained during the same process as the foregoing compound. is a colourless liquid which is very sparingly soluble in water, is freely dissolved by alcohol and ether. It has an ethereal p gent odour and a burning taste, and becomes rapidly conver into butyric acid by exposure to the air. It forms with ammo the crystalline compound characteristic of the aldehyds, and wh heated with a solution of nitrate of silver, gives a brilliant mir of reduced metal. It boils between 154° and 163°.

Butyral (*Sp. gr. of vapour* 2·61; *of liquid at* 71°, 0·821) the name given by Chancel to a compound isomeric with the fo going body, obtained by the distillation of dry butyrate of lim when exposed to the air, it absorbs oxygen and becomes rap converted into butyric acid. It, however, yields no compo with ammonia, and does not reduce the nitrate of silver.

(1082) 5. *Valeric Aldehyd* ($C_{10}H_{10}O_2$); *Sp. gr. of liquid* *of vapour* 2·96; *Boiling pt.* 205°.—This compound may be obta in various ways. One of the best consists in oxidizing fousel by means of a mixture of sulphuric acid and bichromate of potash 37 parts of bichromate of potash dissolved in warm water placed in a retort, are to be gradually mixed with 49 parts o of vitriol, previously diluted with an equal bulk of water; 33 of fousel oil are then to be carefully added: the aldehyd di over without the necessity for applying heat. If the distillat mixed with a saturated solution of bisulphite of soda, the pound of bisulphite of soda and valeric aldehyd crystallizes rea and may be purified by recrystallization from alcohol. If crystals be mixed with a solution of carbonate of potash, and tilled, valeric aldehyd passes over, and may be dried over chl of calcium. This aldehyd is a highly mobile, limpid, colo liquid, with a burning taste and a pungent, penetrating odour vapour takes fire easily. It is insoluble in water, but solub alcohol and in ether. By oxidation it is rapidly converted valeric acid.

proic Aldehyd is scarcely known.

3) 7. *Œnanthylic Aldehyd*, or *Œnanthol* ($C_{14}H_{14}O_2$) : *Sp.* *uid* 0·8271 *at* 63°; *of vapour* 4·17 ; *Boiling pt.* about his aldehyd is furnished by the destructive distillation of . In order to purify the crude distillate, it is agitated ta water, which retains the volatile acids ; the oil, which he surface on standing, is submitted to distillation, and ied by digestion on chloride of calcium. Water dissolves ly. It rapidly absorbs oxygen from the air, and becomes into œnanthylic acid.

) 8. *Caprylic Aldehyd* ($C_{16}H_{16}O_2$) ; *Sp. gr. of liquid* *oiling pt.* 340°.—This is a powerfully refracting, colour-
l, with an odour of banana, and a burning taste. It is in water, and exhibits very little tendency to become but it forms a crystalline compound with the bisulphite , and it reduces nitrate of silver, producing a beautiful e deposit of the metal. It is easily obtained by the dry n of caprylate of soda.

largonic Aldehyd has not been examined.

) 10, 11, and 12. *Capric, Euodic,* and *Lauric Aldehyd.* substances appear to be among the constituents of oil of rhardt considered that it consisted mainly of capric alde-
G. Williams appears to have shown that euodic aldehyd ; *Sp. gr. of liquid* 0·8497 ; *of vapour* 5·87 ; *Freezing pt.* *oil. pt.* 415°·4) is its most abundant component. This oil mewhat viscid consistence ; it possesses the strong dis-
odour of the plant, and an acrid, bitterish, somewhat taste. Nitric acid acts rapidly upon oil of rue, and fur-
ferent products according to the degree of concentration id ; by the prolonged action of the concentrated acid, c acid ($HO,C_{18}H_{17}O_3$), and the lower homologues of the acids to which it belongs are obtained ; by moderating the the nitric acid, capric acid ($HO,C_{20}H_{19}O_3$) is procured. f rue does not absorb oxygen very rapidly, nor is it easily d when heated with hydrate of potash into the caprate of ; but it combines readily with the alkaline bisulphites, s with them crystallizable compounds which correspond e formed with the other aldehyds.

(*b*) *The Ketones, or Acetones.*

6) The ketones constitute a class of compounds closely to the aldehyds.

When the lime or baryta salt of any of the volatile aci normal hydrates of which contain 4 equivalents of oxyg submitted to dry distillation, the acid undergoes decompo and amongst the volatile products which come over, is a which has been termed the *ketone* of the acid: the new which is formed bears the same relation to the acid from it is obtained that acetone does to acetic acid.

The general properties of this class of compounds m illustrated by a description of acetone, which has been ex with care.

(1087) *Acetone* ($C_6H_6O_2$): *Sp. gr. of liquid* 0·792; *of* 2·002; *Boiling pt.* 133°.—When acetate of lime is mixed w excess of quicklime, and submitted to distillation, 2 equi of acetic acid lose 2 equivalents of carbonic acid, and a v inflammable liquid passes over, to which the formula C_6H_6 been assigned:—

$$2\,\overbrace{(CaO,C_4H_3O_3)}^{\text{Acetate of lime.}} = \overbrace{2\,CaO,C_2O_4}^{\text{Carb. of lime.}} + \overbrace{C_6H_6O_2}^{\text{Acetone.}}.$$

When the vapours of acetic acid are transmitted thr heated porcelain tube they are resolved into acetone, carbon and water; $2\,C_4H_4O_4 = C_2O_4 + H_2O_2 + C_6H_6O_2$; but a bette of preparing acetone than either of the foregoing ones con distilling crystallized acetate of lead, with half its weight of lime.

Acetone is a colourless liquid, with an agreeable ethereal and a pungent taste. When heated it gives off an infla vapour, which burns with a clear white flame. When heat hydrate of potash, it yields at a moderate temperature a mi acetate and formiate of potash, with liberation of hydrogen

$$\overbrace{C_6H_6O_2}^{\text{Acetone.}} + 2\,(KO,HO) + H_2O_2 = \overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}} + \overbrace{KO,C_2HO_3}^{\text{Formiate of potash.}} + 3$$

At a higher temperature carbonate of potash and marsh the result:—

$$\overbrace{C_6H_6O_2}^{\text{Acetone.}} + 2\,(KO,HO) = \overbrace{2\,KO,C_2O_4}^{\text{Carb. potash.}} + 2\,\overbrace{C_2H_4}^{\text{Marsh gas.}}.$$

Gerhardt and Chancel consider acetone as a species of in which an atom of hydrogen is displaced by its equiv methyl:*

---

* Some doubt exists as to the true nature of the ketones. Ka species, which has been more thoroughly examined than any of th to a sort of alcohol (C_6H_5O,HO) which he terms *mesitic alcohol;*

Ethylic aldehyd $C_4H_3O_2$, H, being *hydride of acetyl,* and
Acetone being $C_4H_3O_2$, C_2H_3, or *methylide of acetyl.*

ketones resemble the aldehyds in their power of forming talline compounds with the bisulphites of potash and soda.

ny view which is adopted for acetone would be extended to the r members of this group, which are all homologous with it; s:—

etone = $C_6H_6O_2$, or $C_4H_3O_2$, C_2H_3, methylide of acetyl
opione = $C_{10}H_{10}O_2$, „ $C_6H_5O_2$, C_4H_5, ethylide of propionyl
tyrone = $C_{14}H_{14}O_2$, „ $C_8H_7O_2$, C_6H_7, tritylide of butyryl
lerone = $C_{18}H_{18}O_2$, „ $C_{10}H_9O_2$, C_8H_9, tetrylide of valeryl.

The experiments of Williamson appear to show that a series uble ketones may be formed, by distilling mixtures of equi- nt quantities of the homologous salts of lime; for example: by lling a mixture of acetate and valerate of lime in equivalent pro- ons, the compound $C_{12}H_{12}O_2$ $(=C_{10}H_9O_2,C_2H_3)$ is formed:—

$$\overbrace{CaO,C_4H_3O_3}^{\text{Acetate of lime.}}+\overbrace{CaO,C_{10}H_9O_3}^{\text{Valerate of lime.}}=\overbrace{C_{10}H_9O_2,C_2H_3}^{\text{Methylide of valeryl.}}+\overbrace{2\,CaO,C_2O_4}^{\text{Carb. lime.}}.$$

reund has also succeeded in obtaining acetone and propione etically, by decomposing chloride of acetyl by means of zinc- yl and zinc-ethyl; thus—

$$2\overbrace{\begin{pmatrix}C_4H_3O_2\\Cl\end{pmatrix}}^{\text{Chlor. acetyl.}}+\overbrace{\left.\begin{matrix}Zn\\C_2H_3\end{matrix}\right\}_2}^{\text{Zinc-methyl.}}=2\overbrace{\left(\begin{matrix}C_4H_3O_2\\C_2H_3\end{matrix}\right\}}^{\text{Acetone.}}+2\left.\begin{matrix}Zn\\Cl\end{matrix}\right\}.$$

Limpricht, in pursuing this subject, found that by mixing for- e of lime in equivalent proportion with acetate of lime, with ate of lime, with œnanthylate of lime, or with caprylate of lime, distilling,—the corresponding aldehyds, viz., acetic, valeric, thylic and caprylic aldehyds, were formed: the formiate of when distilled, yielding hydrogen instead of C_2H_3, as in Wil- son's experiment:—

$$\overbrace{CaO,C_2HO_3}^{\text{Formiate of lime.}}+\overbrace{CaO,C_4H_3O_3}^{\text{Acetate lime.}}=\overbrace{H,C_4H_3O_2}^{\text{Aldehyd.}}+\overbrace{2\,CaO,C_2O_4}^{\text{Carb. lime.}}.$$

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with allylic alcohol. By distilling it with sulphuric acid he obtained a und having the composition C_6H_5O, which corresponds to the ether of lcohol, and is metameric with allylic ether. He also produced other responding to iodide and chloride of ethyl. Acetone forms with acid, a double acid $(2\,HO,C_6H_5O,S_2O_6)$. But this sulpho-acid is ke the true vinic acids; moreover, acetone cannot be recovered s it is decomposed by the hydrated alkalies; whilst all the true be reproduced from the vinic sulpho-acids when they are decom- manner by the alkalies.

The following results obtained by Stædeler from acetone (*A de Chimie,* III. xlii. 226) have tended to confirm these vi Chlorine forms with acetone various substitution-products, most remarkable of which is one in which five atoms of hydro are displaced by five of chlorine; a compound, $C_6HCl_5O_2$, analog to chloral is thus formed; it has a sp. gr. of from 1·6 to 1·7, not solidified by a cold of —4°, and it boils at about 374°. body has the property of combining with eight equivalents of wa with which it forms a soluble crystallizable substance analogou hydrate of chloral.

Acetone when saturated with gaseous ammonia yields a li which reduces the salts of silver, in a manner similar to the responding mixture with aldehyd. If this acetonic solution ammonia be left to itself for some time, it is spontaneously tr formed into a new base, *acetonine* or *acetonia* ($C_{18}H_{18}N_2$); and same change is effected more rapidly by exposing the mixture some hours in a sealed tube to a heat of 212°. The decomp tion by which it is formed, is similar to that by which benzolin produced from the oil of bitter almonds (1198):—

$$3\overbrace{C_6H_6O_2}^{\text{Acetone.}}+2\,H_3N=\overbrace{C_{18}H_{18}N_2}^{\text{Acetonia.}}+3\,H_2O_2.$$

Acetonia is a colourless alkaline liquid, of a peculiar uri odour, and a burning taste. It is readily soluble in water, alc and ether. Hydrochlorate of acetonia forms with bichlori platinum, an orange-yellow, crystalline double salt ($C_{18}H_{18}N_2$,H $PtCl_2$). The binoxalate ($HO,C_{18}H_{18}N_2,HO,C_4O_6+2Aq$) is so in alcohol, and crystallizes readily from this solution.

Acetone may also be made to furnish an acid homologous the lactic. This compound, termed *acetonic acid* (HO,C may be obtained by heating a mixture of acetone and hy cyanic acid with hydrochloric acid, when the following rea occurs:—

$$\overbrace{C_6H_6O_2}^{\text{Acetone.}}+\overbrace{H,C_2N}^{\text{Hydrocy. acid.}}+2\,H_2O_2+HCl=\overbrace{HO,C_8H_7O_5}^{\text{Acetonic acid.}}+H_4N,Cl.$$

Acetonic acid crystallizes in prisms; it has a sour taste, a freely soluble in water, in alcohol, and in ether. It forms cr lizable salts: the *acetonate of zinc* ($ZnO,C_8H_7O_5+2Aq$) is sparingly soluble. The baryta salt is soluble in alcohol.

The attempt to procure a base homologous with glycocin alanine, by the action of hydrocyanic acid upon acetone unsuccessful.

It is probable that each of the other ketones would yield com-ds analogous to those which Stædeler has procured from ne. Each of the ketones is metameric with a corresponding in the series of true aldehyds; for example:—

Acetone = $C_6H_6O_2$ = Propionic aldehyd.
Propione = $C_{10}H_{10}O_2$ = Valeric aldehyd.
Butyrone = $C_{14}H_{14}O_2$ = Œnanthylic aldehyd.

areful oxidation, Stædeler succeeded in converting acetone propionic acid.

he formation of ketones has also been observed in the case eral monobasic acids which do not belong to the series of the acids. Benzoic acid, for example, is decomposed in the fol-g manner :—

$$2\,\overbrace{(CaO,C_{14}H_5O_3)}^{\text{Benzoate of lime.}} = \overbrace{C_{26}H_{10}O_2}^{\text{Benzone.}} + \overbrace{2\,CaO,C_2O_4}^{\text{Carb. of lime.}}.$$

e products of the distillation of the lime salts of the dibasic such as the suberic acid, do not fall strictly into the class of s. The substance termed *suberone*, for nstance, consists of O_2, instead of $C_{14}H_{12}O_2$.

will be useful here, before passing to the consideration of ecial class of acids produced by the oxidation of the aldehyds sider briefly the general properties of the organic acids, as a and some of the more important groups of derivatives from

§ II. General Remarks on the Organic Acids.

88) The Organic Acids constitute an extremely numerous portant class of compounds; but many of them are so in-y related to a large number of other well-defined natural that it would be far from advantageous to detach each m the group to which it properly belongs, for the sake of ting it with other bodies to which, often, it may bear little lance save in the circumstance that, like them, it possesses power of forming salts with bases. Accordingly, some of bodies have already been described in the previous sections, they seemed to be naturally connected with the compounds examination; and, although it will be convenient to asso-together certain of the acids in the present chapter, the con-on of others will be postponed until the substances to which e most nearly allied pass under review.

At present no organic alkali is known, into the composition h nitrogen does not enter; so that if it be ascertained that nitrogen is absent from any particular compound, it may at once be concluded that the body in question cannot belong to the class of organic bases; but there is no elementary substance with the presence of which the acid character can be thus specifically connected: and no general law of composition has hitherto been arrived at, by which it is rendered possible from a knowledge of the empirical formula of a substance, to predict that it will or will not possess the properties of an acid.

(1089) *Monobasic and Polybasic Acids.*—The organic acids may be subdivided into *monobasic* and *polybasic* (1099); the important group derived from the monobasic alcohols by oxidation, furnishing a good illustration of the monobasic acids; whilst some of the more important and widely diffused vegetable acids, such as the citric, the tartaric, and the malic, afford examples of the polybasic class, and have been traced to the polybasic alcohols.

The following table may serve to illustrate the connexion of several of the most interesting groups of acids, and of their relation to the alcohol groups:—

			Acids.		
		Alcohols.	Monobasic.	Dibasic.	Tribasic.
Monatomic		$\left.\begin{matrix}C_{2n}H_{2n+1}\\H\end{matrix}\right\}O_2$	$\left.\begin{matrix}C_{2n}H_{2n-1}O_2\\H\end{matrix}\right\}O_2$		
	(1)	Wood spirit. $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O_2$	Formic. $\left.\begin{matrix}C_2H\,O_2\\H\end{matrix}\right\}O_2$		
$\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$	(2)	Alcohol. $\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2$	Acetic. $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$		
	(3)	Tritylic alcohol. $\left.\begin{matrix}C_6H_7\\H\end{matrix}\right\}O_2$	Propionic. $\left.\begin{matrix}C_6H_5O_2\\H\end{matrix}\right\}O_2$		
Diatomic.		$\left.\begin{matrix}C_{2n}H_{2n}\\H_2\end{matrix}\right\}O_4$	$\left.\begin{matrix}C_{2n}H_{2n-2}O_2\\H_2\end{matrix}\right\}O_4$	$\left.\begin{matrix}C_{2n}H_{2n-4}O_4\\H_2\end{matrix}\right\}O_4$	
	(2)	Glycol. $\left.\begin{matrix}C_4H_4\\H_2\end{matrix}\right\}O_4$	Glycolic. $\left.\begin{matrix}C_4H_2O_2\\H_2\end{matrix}\right\}O_4$	Oxalic. $\left.\begin{matrix}C_4\quad O_4\\H_2\end{matrix}\right\}O_4$	
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4$	(3)	Tritylglycol. $\left.\begin{matrix}C_6H_6\\H_2\end{matrix}\right\}O_4$	Lactic. $\left.\begin{matrix}C_6H_4O_2\\H_2\end{matrix}\right\}O_4$	Malonic [?] $\left.\begin{matrix}C_6H_2O_4\\H_2\end{matrix}\right\}O_4$	
	(4)	Tetrylglycol. $\left.\begin{matrix}C_8H_8\\H_2\end{matrix}\right\}O_4$	Acetonic. $\left.\begin{matrix}C_8H_6O_2\\H_2\end{matrix}\right\}O_4$	Succinic. $\left.\begin{matrix}C_8H_4O_4\\H_2\end{matrix}\right\}O_4$	

		Acids.		
	Alcohols.	Monobasic.	Dibasic.	Tribasic.
—	$\left.\begin{matrix}C_{2n}H_{2n-1}\\H_3\end{matrix}\right\}O_6$	$\left.\begin{matrix}C_{2n}H_{2n-3}O_2\\H_3\end{matrix}\right\}O_6$	$\left.\begin{matrix}C_{2n}H_{2n-5}O_4\\H_3\end{matrix}\right\}O_6$	
(3)	Glycerin. $\left.\begin{matrix}C_6H_5\\H_3\end{matrix}\right\}O_6$	Glyceric. $\left.\begin{matrix}C_6H_3O_2\\H_3\end{matrix}\right\}O_6$	Tartronic [?] $\left.\begin{matrix}C_6HO_4\\H_3\end{matrix}\right\}O_6$	
(4)			Malic. $\left.\begin{matrix}C_8H_3O_4\\H_3\end{matrix}\right\}O_6$	
nic.	$\left.\begin{matrix}C_{2n}H_{2n-2}\\H_4\end{matrix}\right\}O_8$	$\left.\begin{matrix}C_{2n}H_{2-\,4}O_2\\H_4\end{matrix}\right\}O_8$	$\left.\begin{matrix}C_{2n}H_{2n-6}O_4\\H_4\end{matrix}\right\}O_8$	$\left.\begin{matrix}C_{2n}H_{2n-8}O_6\\H_4\end{matrix}\right\}O_8$
(4)			Tartaric. $\left.\begin{matrix}C_8H_2O_4\\H_4\end{matrix}\right\}O_8$	
(6)				Citric [?] $\left.\begin{matrix}C_{12}H_4O_8\\H_4\end{matrix}\right\}O_8$
nic.	$\left.\begin{matrix}C_{2n}H_{2n-4}\\H_6\end{matrix}\right\}O_{12}$	$\left.\begin{matrix}C_{2n}H_{2n-6}O_2\\H_6\end{matrix}\right\}O_{12}$	$\left.\begin{matrix}C_{2n}H_{2n-8}O_4\\H_6\end{matrix}\right\}O_{12}$	$\left.\begin{matrix}C_{2n}H_{2n-10}O_6\\H_6\end{matrix}\right\}O_{12}$
(6)	Mannite [?] $\left.\begin{matrix}C_{12}H_8\\H_6\end{matrix}\right\}O_{12}$		Saccharic. $\left.\begin{matrix}C_{12}H_4O_4\\H_6\end{matrix}\right\}O_{12}$	

ny attempts have been made, without success, to account polybasic or monobasic character of the acids from their ition. Kekulé has offered the following ingenious suggespon this subject. According to this chemist,—1. Bodies er monatomic or polyatomic, which are formed upon the type er—*i.e.* which are of the form $x\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, which contain only and hydrogen in the radicle that displaces the typical in the molecule, belong to the class of *alcohols*, as for ple—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}\quad ; \quad \overbrace{\left.\begin{matrix}(C_4H_4)''\\H_2\end{matrix}\right\}O_4}^{\text{Glycol.}}\quad ; \quad \overbrace{\left.\begin{matrix}(C_6H_5)'''\\H_3\end{matrix}\right\}O_6}^{\text{Glycerin.}}.$$

Those bodies which in addition to carbon, or to carbon and hydrogen, contain 2 atoms of oxygen in the displacing radicle, constitute well defined monobasic* acids; for example:—

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\ H\end{matrix}\right\}O_2}^{\text{Acetic acid.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_6H_4O_2\\ H_2\end{matrix}\right\}O_4}^{\text{Lactic acid.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_6H_3O_2\\ H_3\end{matrix}\right\}O_6}^{\text{Glyceric acid.}}.$$

They allow *one atom only* of the typical hydrogen in the molecule to be displaced readily by a metal.

3. Those compounds, which contain 4 atoms of oxygen in the displacing radicle, constitute dibasic acids, whether they contain 4, 6 or 8 atoms of oxygen external to the radicle, as for example,—

$$\overbrace{\left.\begin{matrix}C_8H_4O_4\\ H_2\end{matrix}\right\}O_4}^{\text{Succinic acid.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_8H_3O_4\\ H_3\end{matrix}\right\}O_6}^{\text{Malic acid.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_8H_2O_4\\ H_4\end{matrix}\right\}O_8}^{\text{Tartaric acid.}}.$$

The basicity of the acid, therefore, upon this view depends, not upon the molecular constitution of the compound,—for in the case of the three acids last cited, the first is diatomic, the second triatomic, and the third tetratomic,—but on the amount of oxygen in the radicle.

(1090) *Simple, and compound or colligated acids.*—The organic acids may further be regarded as belonging to one or other of the following classes:—

a. Hydrated oxides of organic radicles, and acids derived from them by substitution.

b. Compound or *colligated* acids.

(*a*) *Hydrated Oxides of Organic Radicles.*—Examples of this class occur in cyanic acid [$HO,(C_2N)O$] and in the series of volatile fatty acids (1103), the first member of which is formic acid (HO,C_2HO_3) the last as yet discovered is the melissic ($HO,C_{60}H_{59}O_3$). The fatty acids may be viewed as hydrated oxides of a compound radicle of the form ($C_{2n}H_{2n-1}O_2$); the radicle of formic acid being C_2HO_2, that of acetic acid $C_4H_3O_2$, and so on. Another group which falls under this subdivision, is that represented by the general formula [$HO,(C_{2n}H_{2n-9}O_2)O$], which has been characterized as the group of aromatic acids, and of which benzoic acid is the type.

(*b*) *Compound Acids.*—These acids consist of an organic compound, which may be either acid or neutral in character, united with an acid either of inorganic or organic origin, the properties

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[*] It is obvious that this statement is not universally true. Carbonic acid, which in combination with potash may be represented as $\left.\begin{matrix}C_2O_2\\ K_2\end{matrix}\right\}O_4$ is manifestly dibasic, though it ought to be monobasic by the foregoing rule.

of which are modified. These compound acids may be subdivided into two groups, in the first of which the saturating power of the combining acid is not affected, while in the second it is more or less diminished.

1. *Compound acids in which the capacity of saturation of the components is unchanged.*—An excellent instance of this class is afforded in the case of formobenzoylic acid ($HO,C_2HO_3+C_{14}H_6O_2$). This compound consists of a combination of formic acid with the oil of bitter almonds; the new acid thus formed possesses a saturating power exactly proportioned to the quantity of formic acid which it contains. Acetonic acid ($HO,C_2HO_3,C_6H_6O_2$) is another example of the same kind, consisting of formic acid united with acetone as its *colligate*, or associated organic compound.

2. *Compound acids of diminished basic power.—Sulpho-acids.*—Numerous instances of this kind occur in the colligated sulphuric acids, such as the sulphethylic (HO,C_4H_5O,S_2O_6), and sulpho-glyceric acid ($HO,C_6H_7O_5,S_2O_6$); in these cases the sulphuric acid and the organic group in entering into combination, part with a certain number of atoms of water; the loss of basic power in most instances corresponding to the number of atoms of water which are displaced from the sulphuric acid when the latter is estimated in the form of the normal hydrate.

The formation of the vinic acids from the alcohols (984 *et seq.*), shows one mode in which these bodies are produced, but this series of compounds constitutes but a single subdivision of the colligated sulpho-acids, which recent researches have proved to be very numerous.

1. When sulphuric anhydride is brought into contact with one of the normal or monohydrated monobasic organic acids, whilst the mixture is kept cool artificially, each molecule (S_2O_6) of the anhydride generally combines with one of the organic acid, and a dibasic acid is the result. For example:—

$$\overbrace{HO,C_4H_3O_3}^{\text{Acetic acid.}}+S_2O_6 = 2\,\overbrace{HO,C_4H_2S_2O_8}^{\text{Aceto-sulphuric acid.}}.$$

The following acids belong to this class:—

Aceto-sulphuric acid . .	$2\,HO,C_4\,H_2S_2O_8$
Propio-sulphuric acid . .	$2\,HO,C_6\,H_4S_2O_8$
Butyro-sulphuric acid . .	$2\,HO,C_8\,H_6S_2O_8$
Benzo-sulphuric acid . .	$2\,HO,C_{14}H_4S_2O_8$.

The same compounds may be formed by heating the amides or nitriles of the series with fuming sulphuric acid. Thus, propionitrile yields propiosulphuric acid :—

$$2\,\overbrace{C_6H_5N}^{\text{Propionitrile.}}+2\,H_2O_2+3\,(2\,HO,S_2O_6)=2\,(\overbrace{2\,HO,C_6H_4S_2O_8}^{\text{Propiosulphuric acid.}})+\overbrace{2\,H_4NO,S_2O_6}^{\text{Sulphate of Ammonia.}};$$

and butyramide by similar treatment furnishes butyrosulphuric acid :—

$$2\,\overbrace{C_8H_9NO_2}^{\text{Butyramide.}}+3\,(2\,HO,S_2O_6)=2\,(\overbrace{2\,HO,C_8H_6S_2O_8}^{\text{Butyro-sulphuric acid.}})+2\,\overbrace{H_4NO,S_2O_6}^{\text{Sulphate of ammonia.}}.$$

2. But if the mixture be heated, in addition to these sulpho-acids, a second series of acids is formed, termed by Hofmann and Buckton (*Phil. Trans.*, 1856) *disulpho-acids.* The reaction which occurs is attended with the evolution of carbonic acid; and a compound is produced which belongs to the series immediately below that of the nitrile acted upon; for example :—

$$2\,\overbrace{C_4H_3N}^{\text{Acetonitrile.}}+5\,(2\,HO,S_2O_6)=2\,(\overbrace{2\,HO,C_2H_2S_4O_{10}}^{\text{Disulphometholic acid.}})+2\,C_2O_4+\overbrace{2\,H_4NO,S_2O_6}^{\text{Sulph. ammon.}};$$

$$2\,\overbrace{C_6H_5N}^{\text{Propionitrile.}}+5\,(2\,HO,S_2O_6)=2\,(\overbrace{2\,HO,C_4H_4S_4O_{10}}^{\text{Disulphetholic acid.}})+2\,C_2O_4+2\,H_4NO,S_2O_6.$$

In this manner they obtained the first four terms of the following series; and by treating aniline in a similar manner they also obtained a disulpho-acid from it. The first compound upon this list is identical with Liebig's *methionic acid;* the disulpho-naphthalic acid was discovered previously by Berzelius :—

Disulphometholic acid .	$2\,HO,C_2\,H_2S_4O_{10}$, or $C_2\,H_4\;2\,S_2O_6$
Disulphetholic acid . .	$2\,HO,C_4\,H_4S_4O_{10}$, or $C_4\,H_6\;2\,S_2O_6$
Disulphotritolic acid . .	$2\,HO,C_6\,H_6S_4O_{10}$, or $C_6\,H_8\;2\,S_2O_6$
Disulphobenzolic acid .	$2\,HO,C_{12}H_4S_4O_{10}$, or $C_{12}H_6\;2\,S_2O_6$
Disulphonaphthalic acid .	$2\,HO,C_{20}H_6S_4O_{10}$, or $C_{20}H_8\;2\,S_2O_6$
Disulphanilic acid. .	$2\,HO,C_{12}H_5NS_4O_{10}$, or $C_{12}H_7N\;2\,S_2O_6$.

Irrespective of any theoretical view of the molecular composition of the first four of these bodies, it is clear that they contain the elements of 1 molecule of a hydrocarbon corresponding to marsh gas, with 2 of sulphuric anhydride (S_2O_6); as is represented in the second series of formulæ contained in the table.

3. There can be no doubt of the possibility of forming a monobasic series of sulpho-acids corresponding to these, in which the hydrocarbon has been acted upon by 1 instead of by 2 molecules of sulphuric anhydride. These compounds would have the following composition; but at present only two of them,—viz., sulpho*benzolic* and sulphanilic acid, have actually been obtained :—

Sulphometholic acid . .	$HO,C_2H_3S_2O_5$ or $C_2H_4S_2O_6$
Sulphetholic acid . . .	$HO,C_4H_5S_2O_5$ or $C_4H_6S_2O_6$
Sulphotritolic acid . .	$HO,C_6H_7S_2O_5$ or $C_6H_8S_2O_6$
Sulphobenzolic acid . .	$HO,C_{12}H_5S_2O_5$ or $C_{12}H_6S_2O_6$
Sulphanilic acid . . .	$HO,C_{12}H_6NS_2O_5$ or $C_{12}H_7NS_2O_6$.

4. Certain of these sulpho-acids may be obtained by the direct n of sulphuric anhydride upon the hydrocarbons:—For ex- e, when olefiant gas is subjected to the action of the anhy- , it forms a compound which Magnus termed *sulphate of carbyle* ; this body, when treated with water, forms ethionic or *hethylic* acid. This body is one of the terms of a new of disulpho-acids, which might probably be formed by sub- g the other hydrocarbons homologous with olefiant gas, to r treatment.

The ordinary vinic acids (984) constitute the series of sulpho- produced by the reaction of 1 molecule (S_2O_6) of sulphuric ride upon the alcohol, whilst ethionic acid is one of the corre- ing disulpho-acids produced by the action of 2 molecules of sul- anhydride upon each molecule of the alcohol. Thus it appears ach alcohol may be made to furnish at least 4 different -acids, two of which are monobasic and two dibasic; typified following acids of the ethylic series:—

Sulphetholic acid	$HO,C_4H_5S_2O_5$
Disulphetholic acid . . .	$2\,HO,C_4H_4S_4O_{10}$
Sulphethylic acid	$HO,C_4H_5S_2O_7$
Ethionic (disulphethylic) acid	$2\,HO,C_4H_4S_4O_{12}$

fmann and Buckton conclude, as the general result of ecent investigation of the sulpho-acids (*Proceed. Roy. Soc.* 55)—That all organic molecules, particularly in the nascent appear to be capable of assimilating the elements either r of 2 molecules of sulphuric anhydride. The formation two groups of acids which are thus produced, presents a nalogy with the production of the nitro-substitutes gene- nder the influence of nitric acid. All these compounds erated with the elimination of water.* In the action of cid and sulphuric acid upon benzol, for instance, we have:—

$$\overbrace{C_{12}H_6}^{\text{Benzol.}} + \quad HO,NO_5 \quad = \quad \overbrace{C_{12}H_5NO_4}^{\text{Nitrobenzol.}} + \quad H_2O_2;$$

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s refers, however, to the case in which it is supposed that the reaction ce between oil of vitriol or *hydrated* sulphuric acid and the organic d, and not when the *anhydride is used; as the* equations which fficiently *show.*

$$\overbrace{C_{12}H_6}^{\text{Benzol.}} + 2(HO,NO_5) = \overbrace{C_{12}H_4N_2O_8}^{\text{Dinitrobenzol.}} + 2\,H_2O_2$$

$$C_{12}H_6 + 2\,HO,S_2O_6 = \overbrace{HO,C_{12}H_5S_2O_5}^{\text{Sulpho-benzolic acid.}} + H_2O_2$$

$$C_{12}H_6 + 2(2\,HO,S_2O_6) = 2\,\overbrace{HO,C_{12}H_4S_4O_{10}}^{\text{Disulpho-benzolic acid.}} + 2\,H_2O_2.$$

The action of nitric acid upon organic bodies is by no limited to the production of nitro-compounds correspond nitro-benzol and dinitro-benzol; frequently additional sub are formed, with elimination of six, eight, and in a few cases, even of ten atoms of water. Hitherto, however, no sub have been observed in which the assimilation of sulphuric a gone further than in the disulpho-acids.

Nitro-acids.—When nitric acid unites with an organi the compound which is formed is generally one which result of a simple process of substitution. The change is attended by the separation of water: no apparent decomp occurs in these cases, but the saturating power of the new not increased by the nitrogen and oxygen which have enter its composition. The nitric acid in reality has been p deoxidized; an atom of hydrogen has been removed fr organic acid, and its place has been supplied by an equiva peroxide of nitrogen. For example, when benzoic acid is upon by nitric acid, the change which occurs is the followin

$$\overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}} + HO,NO_5 = \overbrace{HO,C_{14}H_4,NO_4,O_3}^{\text{Nitrobenzoic acid.}} + H_2O_2$$

Many of the nitro-acids obtained in this manner are yello and salts which have a yellow colour; these salts generally and often detonate, when they are exposed to heat; and heated with sulphuric acid and peroxide of manganese the emit nitrous fumes. A few of the best known of these com are enumerated below:—

Dinitrophenic acid . . .	$HO,C_{12}H_3(NO_4)_2O$
Trinitrophenic (carbazotic) .	$HO,C_{12}H_2(NO_4)_3O$
Nitrobenzoic	$HO,C_{14}H_4(NO_4)\,O_3$
Dinitrobenzoic	$HO,C_{14}H_3(NO_4)_2O_3$
Nitrocinnamic	$HO,C_{18}H_6(NO_4)\,O_3$
Nitrosalicylic	$HO,C_{14}H_4(NO_4)\,O_5$
Nitranisic	$HO,C_{16}H_6(NO_4)\,O_5$

([illegible]) *Action of Heat upon the Organic Acids.*—A of the monobasic vegetable acids, the normal hydrates of ontain 4 or 6 atoms of oxygen, may be volatilized without osition; but the greater number of the more complicated ic organic acids are decomposed by the application of heat. f them give rise to acids of simpler composition, which are by the abstraction of the elements of water; or by the l of the elements of carbonic acid; or by the loss of ater and carbonic acid. Several of these new acids are ; others undergo complete decomposition if subjected to a temperature than that at which they were formed:—For le, citric acid by losing the elements of water furnishes ic acid:—

$$3\,\overbrace{HO,C_{12}H_5O_{11}}^{\text{Citric acid.}} = 3\,\overbrace{HO,C_{12}H_3O_9}^{\text{Aconitic acid.}} + H_2O_2;$$

a higher temperature aconitic loses carbonic acid;

$$3\,\overbrace{HO,C_{12}H_3O_9}^{\text{Aconitic acid.}} = 2\,\overbrace{HO,C_{10}H_4O_6}^{\text{Itaconic acid.}} + C_2O_4.$$

he action of a gradually increasing temperature upon tartaric remarkable:—this acid undergoes several different stages of ration, and then loses carbonic acid, in the manner shown subjoined equations:—

$$1)\quad 4\,(\overbrace{2\,HO,C_8H_4O_{10}}^{\text{Tartaric acid.}}) = 2\,(\overbrace{3\,HO,\,2\,C_8H_4O_{10}}^{\text{Tartralic acid.}}) + H_2O_2;$$

$$2)\quad 2\,(\overbrace{3\,HO,\,2\,C_8H_4O_{10}}^{\text{Tartralic acid.}}) = 2\,(\overbrace{2\,HO,\,2\,C_8H_4O_{10}}^{\text{Tartrelic acid.}}) + H_2O_2;$$

$$3)\quad \overbrace{2\,HO,\,2\,C_8H_4O_{10}}^{\text{Tartrelic acid.}} = \overbrace{2\,C_8H_4O_{10}}^{\text{Tartaric anhydride.}} + H_2O_2;$$

$$4)\quad \overbrace{2\,C_8H_4O_{10}}^{\text{Tartaric anhydride.}} = \overbrace{2\,HO,C_{12}H_6O_{10}}^{\text{Pyruvic acid.}} + 2\,C_2O_4;$$

$$5)\quad \overbrace{2\,HO,C_{12}H_6O_{10}}^{\text{Pyruvic acid.}} = \overbrace{2\,HO,C_{10}H_6O_6}^{\text{Pyrotartaric acid.}} + C_2O_4.$$

ain, malic acid, by the loss of water, yields fumaric (para- c) acid;

$$\overbrace{2\,HO,C_8H_4O_8}^{\text{Malic acid.}} = \overbrace{2\,HO,C_8H_2O_6}^{\text{Fumaric acid.}} + H_2O_2;$$

umaric acid by sublimation is converted into its isomeride ic acid.

ke *manner gallic acid by the loss of* 2 equivalents of carbonic acid yields pyrogallic acid; and pyrogallic acid in its turn, by the loss of 2 equivalents of water, furnishes metagallic acid:—

$$\overbrace{3\ \mathrm{HO,C_{14}H_3O_7}}^{\text{Gallic acid.}} = \overbrace{\mathrm{C_{12}H_6O_6}}^{\text{Pyrogallic acid.}} + \mathrm{C_2O_4};$$

$$\overbrace{\mathrm{C_{12}H_6O_6}}^{\text{Pyrogallic acid.}} = \overbrace{\mathrm{C_{12}H_4O_4}}^{\text{Metagallic acid.}} + \mathrm{H_2O_2}.$$

Results closely analogous are afforded by the decomposition of meconic acid; a solution of which, at a temperature not exceeding that of boiling water, is converted into comenic acid by the loss of 2 equivalents of carbonic acid; and comenic acid itself if subjected to distillation loses 2 equivalents of carbonic acid, and furnishes another distinct volatile acid, the pyromeconic:—

$$\overbrace{3\ \mathrm{HO,C_{14}H_3O_{11}}}^{\text{Meconic acid.}} = \overbrace{2\ \mathrm{HO,C_{12}H_2O_8}}^{\text{Comenic acid.}} + \mathrm{C_2O_4};$$

$$\overbrace{2\ \mathrm{HO,C_{12}H_2O_8}}^{\text{Comenic acid.}} = \overbrace{\mathrm{HO,C_{10}H_3O_5}}^{\text{Pyromeconic acid.}} + \mathrm{C_2O_4}.$$

(1092) *Effects of Chlorine, &c., upon the Acids.*—Chlorine generally acts upon the monobasic acids simply by displacing hydrogen, thus producing a body of the same chemical type as the original acid, and containing the same number of elements similarly arranged. In the radicle of acetic acid, for instance, the 3 atoms of hydrogen may be displaced by 3 of chlorine; and trichloracetic acid, which is analogous to the original acetic acid, is produced; $\mathrm{HO,C_4H_3O_3} + 3\ \mathrm{Cl_2} = \mathrm{HO,C_4Cl_3O_3} + 3\ \mathrm{HCl}$. By a substitution of a similar kind, benzoic acid ($\mathrm{HO, C_{14}H_5O_3}$) yields chlorobenzoic acid, $\mathrm{HO, C_{14}H_4ClO_3}$. In other instances, especially in the more complex acids, the original group of elements is broken up into two or more groups of similar constitution. Thus citric acid ($3\ \mathrm{HO, C_{12}H_5O_{11}}$), when treated with chlorine, yields a neutral chlorinated body ($\mathrm{C_8Cl_6O_3}$), besides other products. The action of bromine and of iodine is analogous to that of chlorine, but with differences depending chiefly upon the feebler character of their affinities. Peroxide of nitrogen may also be substituted for a part of the hydrogen, equivalent for equivalent; but in this case the acid character of the nitric acid whence the peroxide was derived, entirely disappears.

It is remarkable that several of the hydrated organic acids have a composition identical with that of anhydrous glucose, *if the ultimate* analysis only be considered; thus furnishing addiional evidence that chemical character depends quite as much ipon the mode of arrangement among the elements, as upon the iature of those elements themselves:—

$$3\,\overbrace{(HO,C_4H_3O_3)}^{\text{3 Ats. Acetic acid.}} = 2\,\overbrace{(HO,C_6H_5O_5)}^{\text{2 Ats. Lactic acid.}} = \overbrace{C_{12}H_{12}O_{12}}^{\text{1 At. Glucose.}}.$$

Many of the acids contain oxygen and hydrogen in exactly the proportions required to form water: such, for example, as the lactic, the acetic, the quinic, the pyrotartaric, and some others.

(1093) *Combined Action of Heat and Bases on the Acids.*—Many of the organic acids when fused with the hydrate of potash are decomposed by it into acetic and oxalic acid, with separation of water, and sometimes with evolution of hydrogen; for example:—

$$2\,\overbrace{HO,C_8H_4O_8}^{\text{Malic acid.}}+3\,(KO,HO) = 2\,\overbrace{KO,C_4O_6}^{\text{Oxalate of potash.}}+\overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}}+2\,H_2O_2+H_2;$$

$$2\,\overbrace{HO,C_{12}H_8O_{14}}^{\text{Mucic acid.}}+4\,(KO,HO) = 2\,\overbrace{KO,C_4O_6}^{\text{Oxalate of potash.}}+2\,\overbrace{(KO,C_4H_3O_3)}^{\text{Acetate of potash.}}+4\,H_2O_2.$$

When the salts of any of the monobasic acids, which in their state of normal hydrates contain 4 equivalents of oxygen, are distilled with hydrate of baryta, they undergo a peculiar decomposition, carbonic acid is retained by the baryta, and a hydro-carbon is given off; for example:—

$$2\,\overbrace{(NaO,C_4H_3O_3)}^{\text{Acetate of soda.}}+2\,(HO,BaO) = 2\,\overbrace{C_2H_4}^{\text{Marsh gas.}}+2\,NaO,C_2O_4+2\,BaO,C_2O_4;$$

$$2\,\overbrace{(CaO,C_{14}H_5O_3)}^{\text{Benzoate of lime.}}+2\,(HO,BaO) = 2\,\overbrace{C_{12}H_6}^{\text{Benzol.}}+2\,CaO,C_2O_4+2\,BaO,C_2O_4.$$

In this manner the salts of the following acids may be decomposed:—

Toluic acid . . .	$HO,C_{16}H_7O_3$,	yielding	Toluol . . .	$C_{14}H_8$
Cinnamic acid . .	$HO,C_{18}H_7O_3$,	,,	Cinnamol . .	$C_{16}H_8$
Cuminic acid . .	$HO,C_{20}H_{11}O_3$,	,,	Cumol . . .	$C_{18}H_{12}$.

When the salts of acids, which in the state of normal hydrates contain 6 equivalents of oxygen, are similarly treated, oxidized compounds are obtained, and a carbonate of the base remains in the retort, as in the former case:—

$$2\,\overbrace{(NaO,C_{16}H_7O_5)}^{\text{Anisate of soda.}}+2\,(HO,BaO) = 2\,NaO,C_2O_4+2\,BaO,C_2O_4+2\,\overbrace{C_{14}H_8O_2}^{\text{Anisol.}};$$

$$2\,\overbrace{(CaO,C_{14}H_5O_5)}^{\text{Salicylate of lime.}}+2\,(HO,BaO) = 2\,CaO,C_2O_4+2\,BaO,C_2O_4+2\,\overbrace{C_{12}H_6O_2}^{\text{Phenol.}}.$$

Reference has already *been made to* the ketones, which are the result of submitting the lime or baryta salt of any of t acids (the normal hydrates of which contain 4 equi oxygen), to dry distillation (1086).

a. Oxychlorides of the Acids.

(1094) *Oxychlorides of the Monobasic Acids.*—Th the lower members of the series HO, $C_{2n}H_{2n-1}O_3$, can made to furnish volatile compounds in which one equ oxygen, as contained in the anhydrous acid, has its plac by chlorine. With acetic acid (HO, $C_4H_3O_3$), an *ac chloride* may be obtained, consisting of $C_4H_3O_2Cl$. In these compounds Gerhardt (*Ann. de Chimie*, III. xx heats together a mixture of 1 atom of the oxychlorid phorus (379) with 3 atoms of the anhydrous potash or of the acid. For instance :—

$$3\,(\overbrace{NaO,C_8H_7O_3}^{\text{Butyrate of soda.}})+\overbrace{PO_2Cl_3}^{\text{Oxychlor. phosph.}}=3\,\overbrace{NaO,PO_5}^{\text{Phosph. of soda.}}+3\,\overbrace{C_8H_7O_2Cl.}^{\text{Butyric oxychloride.}}$$

In some cases it is more advantageous to mix tercl phosphorus with the monohydrated acid, in the propor atoms of the acid to 1 atom of the terchloride of ph In the case in which acetic acid is employed, the reac follows :—

$$2\,(\overbrace{HO,C_4H_3O_3}^{\text{Acetic acid.}})+PCl_3=HO,PO_3+HCl+2\,\overbrace{C_4H_3O_2Cl}^{\text{Acetic oxychlori}}$$

and on distilling the mixture, the new compound pas whilst phosphorous acid remains in the retort. By thes the following oxychlorides have been prepared :—

Oxychlorides.	Formulæ.	Boiling Point ° F.	Sp Li
Acetic oxychloride . . .	$C_4H_3O_2Cl$	131	1·1
Propionic ,, ...	$C_6H_5O_2Cl$	176	
Butyric ,, ...	$C_8H_7O_2Cl$	203	
Valeric ,, ...	$C_{10}H_9O_2Cl$	239—248	1·
Pelargonic ,, ...	$C_{18}H_{17}O_2Cl$	428	

One molecule of each of these bodies yields four v vapour. The vapour of these compounds is extremely to the lungs, and their manipulation consequently dema care, otherwise the health of the operator would be ser dangered. Water immediately decomposes these oxychlorides into the hydrated acid and free hydrochloric acid. The action of a few drops of water upon acetic oxychloride is so violent as to amount to an explosion; $C_4H_3O_2Cl + H_2O_2$ becoming $HO, C_4H_3O_3 + HCl$. Oxychlorides corresponding to the foregoing compounds may also be obtained with the aromatic acids, such as the benzoic, toluic, cinnamic, and cuminic acids:—

Oxychlorides.	Formulæ.	Boiling point. °F.	Specific Gravity.	
			Liquid.	Vapour.
Benzoic oxychloride	$C_{14}H_5O_2Cl$	385	1·25	4·987
Toluic "	$C_{16}H_7O_2Cl$	419	1·175	
Cinnamic "	$C_{18}H_7O_2Cl$	502	1·207	
Cuminic "	$C_{20}H_{11}O_2Cl$	495	1·070	
Anisic "	$C_{16}H_7O_4Cl$	504	1·261	

(Cahours, *Ann. de Chimie*, III. xxiii. 337).

These oxychlorides, though unimportant in themselves, have in the hands of Gerhardt, led to the discovery of a general method of procuring the anhydrides of the acids from which they are derived (1096).

If oxybromide of phosphorus be used instead of the oxychloride for decomposing the salt of the organic acid, oxybromides of corresponding composition may be procured.

(1095) *Oxychlorides of the dibasic acids*, such as the succinic oxychloride ($C_8H_4O_4Cl_2$), and citraconic oxychloride ($C_{10}H_4O_4Cl_2$), may also be procured; but it is best in these cases to act upon the anhydrides of these acids with the perchloride of phosphorus: they are obtained in a state of purity with difficulty, since they are generally decomposed at a temperature below their point of volatilization.

b. The Anhydrides, or Anhydrous Acids.

(1096) The oxychlorides of the monobasic acids may be employed to furnish the anhydrides of their respective acids, by causing an equivalent of the oxychloride to decompose an equivalent of the dry potash or soda salt of the acid to which it corresponds. For instance, in the preparation of acetic anhydride, an equivalent of acetic oxychloride is treated with an equivalent of anhydrous acetate of potash, when the following reaction occurs:—

$$\overbrace{C_4H_3O_2Cl}^{\text{Acetic oxychloride.}} + \overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}} = KCl + \overbrace{C_4H_3O_3,C_4H_3O_3}^{\text{Acetic anhydride.}}.$$

It is not necessary to isolate the oxychloride in order to procure the anhydride of the acid, for if one atom of oxychloride of phosphorus be made to act upon six atoms of the anhydrous salt, instead of upon three atoms, as would be required in the preparation of the oxychloride of the organic acid, a compound reaction occurs. The oxychloride of the acid is first formed, and this body in the moment of its formation reacts upon the excess of the salt employed, and the anhydride is at once liberated. For example, in the preparation of acetic anhydride, these two stages would be thus indicated :—

$$(1)\quad \overbrace{PO_2Cl_3}^{\text{Oxychlor. phosph.}} + \overbrace{3\,(KO,C_4H_3O_3)}^{\text{Acetate of potash.}} = 3\,KO,PO_5 + \overbrace{3\,C_4H_3O_2Cl}^{\text{Acetic oxychloride.}};$$

$$(2)\quad \overbrace{3\,C_4H_3O_2Cl}^{\text{Acetic oxychloride.}} + \overbrace{3\,(KO,C_4H_3O_3)}^{\text{Acetate of potash.}} = 3\,KCl + \overbrace{3\,(C_4H_3O_3,C_4H_3O_3)}^{\text{Acetic anhydride.}}.$$

Or the whole may be comprehended in a single equation such as the following, which represents the preparation of valeric anhydride :—

$$\overbrace{PO_2Cl_3}^{\substack{\text{Oxychl.}\\ \text{phosph.}}} + 6\,\overbrace{(KO,C_{10}H_9O_3)}^{\text{Valerate of potash.}} = 3\,KO,PO_5 + 3\,KCl + \overbrace{3\,(C_{10}H_9O_3.C_{10}H_9O_3)}^{\text{Valeric anhydride.}}.$$

Gerhardt and Chiozza have thus obtained, amongst others, the anhydrides of the following acids :—

Anhydrides.	Formulæ.	Boiling point ° F.	Specific Gravity.	
			Liquid.	Vapour.
Acetic	$(C_4H_3O_3,C_4H_3O_3)$	280	1·073	3·47
Butyric . . .	$(C_8H_7O_3,C_8H_7O_3)$	374	0·978	5·38
Valeric . . .	$(C_{10}H_9O_3.C_{10}H_9O_3)$	419	0·934	6·23
Caproic . . .	$(C_{12}H_{11}O_3.C_{12}H_{11}O_3)$			
Œnanthylic . .	$(C_{14}H_{13}O_3.C_{14}H_{13}O_3)$		0·92	
Caprylic . . .	$(C_{16}H_{15}O_3.C_{16}H_{15}O_3)$	about 536		
Pelargonic . .	$(C_{18}H_{17}O_3.C_{18}H_{17}O_4)$			

These anhydrides assume the form of neutral oily bodies, which are insoluble in water, but which by contact with this liquid are gradually converted into the corresponding hydrated acids. They are susceptible of volatilization without undergoing decomposition. They possess, in many cases, an odour distinct from that of the hydrated acids to which they give rise. In entering into combination with ammonia, they form amides or salts of amidated acids (1166).

But the mode in which these compounds are formed is of greater interest to chemical theory than the mere fact of their existence. They are formed, it will be observed, not by the *abstraction of* water from the hydrated acids, nor by the removal of a metallic oxide from one of the salts of the acid, but by a true process of substitution, so that the anhydrides of these monobasic acids cannot be accurately represented by any formula which would indicate that they consisted of a salt deprived of its base, or of a hydrate deprived of its water. For example, normal acetic acid in its most concentrated form, is represented as $HO, C_4H_3O_3$, and acetate of potash is $KO, C_4H_3O_3$, but acetic anhydride is not simply $C_4H_3O_3$. It is truly $C_4H_3O_3, C_4H_3O_3$, since it is formed by substituting an equivalent of $C_4H_3O_2$, in the place of an equivalent of hydrogen or of potassium :—

$$\overbrace{KO, C_4H_3O_3}^{\text{Acetate of potash.}} + \overbrace{(C_4H_3O_2)Cl}^{\text{Acetic oxychloride.}} = \overbrace{(C_4H_3O_3, C_4H_3O_3)}^{\text{Acetic anhydride.}} + KCl.$$

The normal (1107) specific gravity of the vapour of monohydrated acetic acid (at 482° F.) is 2·080; that is to say, 1 molecule yields 4 volumes of vapour: whilst the vapour-density of the anhydride is 3·47,—consequently its molecule (supposing it to yield 4 volumes of vapour) must be represented by the formula $(C_4H_3O_3, C_4H_3O_3)$. But the following proof of the correctness of the theory of this duplicate composition of the anhydrides, will, perhaps, by many be esteemed still more convincing.

(1097) *Double* or *Mixed Anhydrides.*—The anhydrides already enumerated are not the only ones which Gerhardt succeeded in obtaining. Benzoic, cinnamic, and cuminic oxychlorides may be procured, by processes analogous to those already described for the preparation of the acetic and other oxychlorides; and the corresponding anhydrides were obtained by employing these oxychlorides to decompose the anhydrous salts of benzoic, cinnamic, and cuminic acids :—

	Oxychlorides.	Anhydrides.
Benzoic	$C_{14}H_5O_2Cl$	$(C_{14}H_5O_3, C_{14}H_5O_3)$
Cinnamic	$C_{18}H_7O_2Cl$	$(C_{18}H_7O_3, C_{18}H_7O_3)$
Cuminic	$C_{20}H_{11}O_2Cl$	$(C_{20}H_{11}O_3, C_{20}H_{11}O_3)$
Nitrobenzoic . . .	$C_{14}\left.\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_2Cl$	$(C_{14}\left.\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_3, C_{14}\left.\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_3)$
Salicylic	$C_{14}H_5O_4Cl$	$(C_{14}H_5O_5, C_{14}H_5O_5)$

Gerhardt, however, did not stop here; he employed the oxychlorides already described, to decompose the salts of *other* acids. Thus benzoic oxychloride was made to decompose dry cuminate of soda, and in this manner a *benzo-cuminic* anhydride was obtained by the following reaction :—

$$\underbrace{C_{14}H_5O_2Cl}_{\text{Benzoic oxychloride.}}+\underbrace{NaO,C_{20}H_{11}O_3}_{\text{Cuminate of soda.}}=NaCl+(\underbrace{C_{14}H_5O_3.C_{20}H_{11}O_3}_{\text{Benzo-cuminic anhydride.}}).$$

By decomposing cinnamate of soda by benzoic oxychlo
benzo-cinnamic anhydride was obtained: and by similar me
the various compounds enumerated in the following list
procured:—

Benzo-cuminic anhydride	$C_{14}H_5O_3.C_{20}H_{11}O_3$
Benzo-cinnamic anhydride.	$C_{14}H_5O_3.C_{18}H_7O_3$
Benzo-benzoic anhydride	$C_{14}H_5O_3.C_{14}H_5O_3$
Benzo-acetic anhydride	$C_{14}H_5O_3.C_4H_3O_3$
Cinnamo-acetic anhydride	$C_{18}H_7O_3.C_4H_3O_3$
Benzo-nitro-benzoic anhydride	$C_{14}H_5O_3.C_{14}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}$
Benzo-salicylic anhydride	$C_{14}H_5O_3.C_{14}H_5O$
Aceto-salicylic anhydride	$C_4H_3O_3.C_{14}H_5O$
Benzo-valeric anhydride	$C_{14}H_5O_3.C_{10}H_9O_3$

These compounds are liquid at ordinary temperatures,
assume the form of neutral oils, which are heavier than wat
left in contact with water they are gradually converted into a
ture of the two monohydrated acids from which they are der
benzo-acetic anhydride, for instance, combining with two eq
lents of water, and forming a mixture of normal benzoic and
acids. If it be attempted to submit these double anhydrid
distillation, they become decomposed, and are generally re
into their component anhydrides. It is obvious that the
going list might be increased almost indefinitely, were the
inducement to add to the number of these compounds;
sically they are unimportant, but the interesting point wh
indicated by their discovery, is the fact that the anhydrides
monobasic acids are really complex bodies, resulting from
combination of two substances of similar composition: the
benzoic anhydride, or benzo-benzoic compound, which
third upon the foregoing list, being perfectly analogous
only in its mode of formation, but also in its properties,
other bodies with which it is associated; it is, however,
stable than they are, and can be distilled without expe
decomposition.

(1098) *Anhydrides of the Dibasic Acids.*—With the
acids the case is different. The anhydrides of these co
can often be obtained from the hydrated acids, by the sim
plication of heat to these bodies, or by distilling them with
drating agents, such as phosphoric anhydride. In this
for instance, chemists have been enabled to procure the f
anhydrides of dibasic acids:—

Succinic anhydride .	$C_8H_4O_6$,	Citraconic . . .	$C_{10}H_4O_6$,
Malæic	$C_8H_2O_6$,	Phthalic . . .	$C_{16}H_4O_6$,
Tartaric	$C_8H_4O_{10}$,	Camphoric . .	$C_{20}H_{14}O_6$.
Pyrotartaric . . .	$C_{10}H_6O_6$,		

These being residues of dibasic acids are already *double* anhydrides, and it will be observed that in every case the number of atoms of each element is divisible by two. Succinic anhydride, for instance, may still be represented as formed upon the type of the double atom of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, thus $\left.\begin{matrix}C_4H_2O_2\\C_4H_2O_2\end{matrix}\right\}O_2$; and the same may be said of tartaric anhydride, $\left.\begin{matrix}C_4H_2O_4\\C_4H_2O_4\end{matrix}\right\}O_2$, and indeed of all the others.

It is worthy of remark, that these dibasic acids are the only acids which form vinic or ethylic acids, such as sulphethylic, oxalethylic, and tartrethylic: and it is they only that can furnish the amidated acids, such as the sulphamic, oxamic, and tartramic acids.

If instead of causing an oxychloride of a monobasic acid to act upon one of the salts of another monobasic acid (as when benzoic oxychloride (chloride of benzoyl) is made to act upon dry acetate of potash), the oxychloride be made to act upon the corresponding salt of a dibasic acid, a double anhydride is not formed, but a mixture of two separate anhydrides is the result. Thus, if benzoic oxychloride be made to act upon dry succinate of soda, a mixture of succinic and benzoic anhydrides is obtained. This result may be explained as follows:—

Each atom of the salt of a dibasic acid contains within itself two atoms of a metallic oxide, in addition to the elements of the corresponding anhydride; there are consequently two stages in the reaction. In the first of these stages the oxychloride decomposes the salt into the anhydride, and into a new salt of the monobasic acid corresponding to the oxychloride used; and in the second stage, this newly formed salt is in its turn decomposed by an additional quantity of the oxychloride, as in the case of the monobasic salts where this latter reaction is the only one which occurs.* For example:—

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* Upon Gerhardt's theory, the sole difference between the anhydrides of the dibasic and of the monobasic acids, (for example, between succinic and acetic anhydrides, supposing them both to be compared with the molecule of water taken as $\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta$), is, that the two molecules of hydrogen assumed by Gerhardt to exist *in the molecule of water, are* displaced in the dibasic anhy-

$$\text{1st stage; } \overbrace{C_{14}H_5O_2Cl}^{\text{Benzoic oxychloride.}} + 2\,\overbrace{NaO,C_8H_4O_6}^{\text{Succinate of soda.}} = \overbrace{C_8H_4O_6}^{\text{Succinic anhydride.}} + NaCl + \overbrace{NaO,C_{14}H_5O_3}^{\text{Benzoate of soda.}};$$

$$\text{2nd stage; } \overbrace{C_{14}H_5O_2Cl}^{\text{Benzoic oxychloride.}} + \overbrace{NaO,C_{14}H_5O_3}^{\text{Benzoate of soda.}} = \overbrace{C_{14}H_5O_3,C_{14}H_5O_3}^{\text{Benzoic anhydride.}} + NaCl.$$

The action of perchloride of phosphorus upon the hydrated acids affords a means of distinguishing between the dibasic and the monobasic acids. In both cases the oxychloride of the acid is formed, but in the case of the dibasic acids the reaction occurs in two stages, in the first of which the anhydride of the acid is produced, whilst in the second stage this anhydride passes into the oxychloride; but with the monobasic acids there is only one stage: hydrated succinic acid, for example, thus yields in the first place anhydrous succinic acid, hydrochloric acid, and oxychloride of phosphorus; and in the second stage of the reaction with an additional quantity of the perchloride of phosphorus, oxychloride of phosphorus, and succinic oxychloride, are formed:—

$$\text{1st stage; } 2\,\overbrace{HO,C_8H_4O_6}^{\text{Succinic acid.}} + \overbrace{PCl_2Cl_3}^{\text{Perchlor. phosph.}} = \overbrace{C_8H_4O_6}^{\text{Succinic anhydride.}} + \overbrace{PO_2Cl_3}^{\text{Oxychlor. phosph.}} + 2\,HCl;$$

$$\text{2nd stage; } \overbrace{C_8H_4O_6}^{\text{Succinic anhydride.}} + PCl_2Cl_3 = \overbrace{C_8H_4O_4Cl_2}^{\text{Succinic oxychloride.}} + PO_2Cl_3.$$

Perchloride of phosphorus never yields the anhydride of a monobasic acid by acting upon the hydrated acid; but the corresponding oxychloride is formed at once, whilst oxychloride of phosphorus and hydrochloric acid are liberated. Thus:—

$$\overbrace{HO,C_4H_3O_3}^{\text{Acetic acid.}} + PCl_2Cl_3 = \overbrace{C_4H_3O_2Cl}^{\text{Acetic oxychloride.}} + HCl + PO_2Cl_3.$$

(1099) *Gerhardt's Theory of the composition of the Monobasic and Dibasic Acids.*—The important experiments which have just been detailed, have given great additional probability to a theory of the constitution of organic compounds, long advocated by Laurent and Gerhardt, already alluded to (918), but which it may be useful to consider in its application to the monobasic and dibasic acids. The basis of this remarkable theory is, that the *normal acids*, or hydrated acids as they are usually termed, are formed upon the type of the molecule of water, which molecule is

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dride by a single indivisible group (such as $\text{Ȼ}_4H_4\text{Ɵ}_2 = C_8H_4O_4$), whilst in the monobasic anhydride this displacement is effected by two identical groups, (such as $\text{Ȼ}_2H_3\text{Ɵ} = C_4H_3O_2$), which need not coexist in the compound, but one of which can be exchanged for another similar or corresponding group.

supposed to consist of $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\text{Ɵ}$: the atomic number of oxygen being double of that generally admitted. It is assumed that hydrogen (as well as the elementary bodies generally) is incapable of existing in a separate form, except in the condition of the double atom $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}$. This molecule or double atom, however, is divisible when in the act of entering into combination; the divisibility being evidenced by the circumstance that one atom (H) admits of being displaced by an atom of some other body, or group of bodies, which represents hydrogen when in combination. In the hydrated monobasic acids, such a substitution is supposed to have occurred, acetic hydrate (monohydrated acetic acid) being represented as $\left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_3\text{Ɵ}\\\mathrm{H}\end{matrix}\right\}\text{Ɵ}$; the group $\text{Ꞓ}_2\mathrm{H}_3\text{Ɵ}$ occupying the place of one of the atoms of hydrogen in the atom of water ($\mathrm{H}_2\text{Ɵ}$). If the place of the second atom of hydrogen in the typical atom of water be occupied by a metal, a *salt* of the acid is formed; thus, acetate of potash would be $\left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_3\text{Ɵ}\\\mathrm{K}\end{matrix}\right\}\text{Ɵ}$; in which an atom of potassium has been substituted for the second atom of hydrogen. Further, if the second atom of hydrogen be displaced by a second group, similar to that which occupies the place of the first, the *anhydride* of the acid is obtained; thus acetic anhydride would be $\left.\begin{matrix}\text{Ꞓ}_2\mathrm{H}_3\text{Ɵ}\\\text{Ꞓ}_2\mathrm{H}_3\text{Ɵ}\end{matrix}\right\}\text{Ɵ}$; in which the position of both the atoms of hydrogen in the typical atom of water, is occupied by the group $\text{Ꞓ}_2\mathrm{H}_3\text{Ɵ}$.

The normal hydrates of the dibasic acids are supposed to have a different constitution; for in them a single indivisible group of atoms is considered to be combined with an atom of water; succinic hydrate, for instance, being $\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\text{Ɵ}, \text{Ꞓ}_4\mathrm{H}_4\text{Ɵ}_3$. When one of the atoms of the hydrogen contained in the basic atom of water is displaced by a single equivalent of a metal, an acid salt is formed: acid succinate of soda, for instance, being $\left.\begin{matrix}\mathrm{Na}\\\mathrm{H}\end{matrix}\right\}\text{Ɵ}, \text{Ꞓ}_4\mathrm{H}_4\text{Ɵ}_3$; and when the second atom of hydrogen is displaced by a second equivalent of a metal, a normal salt of the dibasic acid is produced; succinate of potash and magnesia, for instance, being $\left.\begin{matrix}\mathrm{K}\\\mathrm{Mg}\end{matrix}\right\}\text{Ɵ}, \mathrm{C}_4\mathrm{H}_4\text{Ɵ}_3$. Further, when the atom of water is abstracted altogether, the anhydride of the acid is left:—succinic anhydride thus consists simply of the hydrated acid deprived of its atom of basic water; $\left.\begin{matrix}H\\H\end{matrix}\right\}Θ$, $Ꞓ_4H_4Θ_3$, becoming separated into $\left.\begin{matrix}H\\H\end{matrix}\right\}Θ$, and $Ꞓ_4H_4Θ_3$.

This theory has the merit of accounting for the necessity of forming the anhydrides of the monobasic acids by substitution; whilst it also explains the possibility of procuring the anhydrides of the dibasic acids by simple dehydration.

The dibasic acids are further distinguished from the monobasic by differences in the vapour volume of the derivatives of the two classes. Thus if equal volumes of the ethers, or of the oxychlorides of the dibasic acids be compared with corresponding compounds of the monobasic series, the proportion of ether or of chlorine contained in compounds assumed to be dibasic will be double of that contained in their correlative monobasic compounds. For example the following formulæ represent equal volumes of vapour:—

Methyl-acetic ether (monobasic)	$\left.\begin{matrix}Ꞓ_2H_3Θ\\Ꞓ\,H_3\end{matrix}\right\}Θ$
Methyl-sulphuric ether (dibasic)	$\left.\begin{matrix}Ꞓ\,H_3\\Ꞓ\,H_3\end{matrix}\right\}Θ,\ SΘ_3$
Acetic oxychloride (monobasic)	$\left.\begin{matrix}Ꞓ_2H_3Θ\\Cl\end{matrix}\right\}$
Sulphuric oxychloride (chloro-sulphuric acid) dibasic	$\left.\begin{matrix}SΘ_2\\Cl_2\end{matrix}\right\}$.

In order that a clearer idea may be obtained of the difference between Gerhardt's view and the one usually adopted by chemists, we subjoin an example of the application of the formulæ of both theories to acetic acid, which has been selected as the type of a monobasic acid; and to succinic acid, which may serve as the type of a dibasic acid.*

Monobasic acid.	Ordinary view.	Gerhardt.
Hydric acetate, or hydrated acetic acid	$HO,C_4H_3O_3$	$\left.\begin{matrix}Ꞓ_2H_3Θ\\H\end{matrix}\right\}Θ$
Potassic acetate, or acetate of potash	$KO,C_4H_3O_3$	$\left.\begin{matrix}Ꞓ_2H_3Θ\\K\end{matrix}\right\}Θ$
Acetic acetate, or anhydrous acetic acid	$C_4H_3O_3,C_4H_3O_3$	$\left.\begin{matrix}Ꞓ_2H_3Θ\\Ꞓ_2H_3Θ\end{matrix}\right\}Θ$

---

* Although acetic acid, and the acids of the series to which it belongs are regarded as monobasic, it must not be forgotten that a large number of these acids form acid salts with potash, such as biformiate, binacetate, and bistearate *of potash.* The cause of this formation of acid salts by acids reputed *to be monobasic,* still requires further researches for its elucidation.

basic acid.	Ordinary view.	Gerhardt.
ydrate, or hy- uccinic acid . .	$2\,HO,C_8H_4O_6$	$\left.\begin{matrix}H\\H\end{matrix}\right\}\text{Ɵ},\text{Ꞓ}_4H_4\text{Ɵ}_3$
nate of soda . .	$NaO,HO,C_8H_4H_6$	$\left.\begin{matrix}H\\Na\end{matrix}\right\}\text{Ɵ},\text{Ꞓ}_4H_4\text{Ɵ}_3$
ccinate of soda .	$2\,NaO,C_8H_4O_6$	$\left.\begin{matrix}Na\\Na\end{matrix}\right\}\text{Ɵ},\text{Ꞓ}_4H_4\text{Ɵ}_3$
ccinate of mag- d potash . . .	$KO,MgO,C_8H_4O_6$	$\left.\begin{matrix}K\\Mg\end{matrix}\right\}\text{Ɵ},\text{Ꞓ}_4H_4\text{Ɵ}_3$
hydride . . .	$C_8H_4O_6$	$\text{Ꞓ}_4H_4\text{Ɵ}_3$

Organic Peroxides.—The foregoing theory of the ids, which represents them as formed upon the model of received further confirmation from Brodie's discovery of organic peroxides corresponding to peroxide of hydrogen. *Roy. Soc.*, ix. 361.)

peroxides may be obtained by decomposing the organic s or oxychlorides by means of pure peroxide of barium. xide of barium must be procured by dissolving the ordixide in hydrochloric acid, then precipitating by baryta l drying the precipitate *in vacuo* over sulphuric acid. o illustrations of these compounds may be admitted here. *ic Peroxide* $[(C_{14}H_5O_2)_2O_4]$ is procured by mixing equiantities of benzoic oxychloride and peroxide of barium in A solid is obtained, which is freely soluble in ether, from s deposited in large brilliant crystals. When heated to a nd 212° it is decomposed with a slight explosion and with carbonic acid. If boiled with a solution of potash, oxygen , and benzoate of potash formed.

c Peroxide $[(C_4H_3O_2)_2O_4]$ may be procured in like mancomposing acetic anhydride with an equivalent quantity le of barium in anhydrous ether. The mixture must be owly, as the reaction is attended with evolution of much he ethereal solution is filtered from the acetate of baryta rated at a low temperature, and the residual fluid washed nes with water. The viscid liquid thus obtained is the of acetyl. It has a burning taste like cayenne pepper: with an aqueous solution of sulphate of indigo, it immescharges the colour. It converts protoxide into peroxide nese, and the yellow into the red prussiate of potash. ater decomposes it, forming acetate of baryta and peroxide ; a single drop placed in a watch-glass and heated, exth a loud report, *shattering the glass to* pieces. The f *water and the peroxide of hydrogen* to the organic

Derivatives of Monobasic Acids ($C_{2n}H_{2n}O_4$).

Aldehyd.	Ketone.	Oxychloride.	Radicle.	Hydrated acid.	Salt.	Anhydride.	Peroxide.
$\left.\begin{array}{l}C_{2n}H_{2n-1}O_2\\H\end{array}\right\}$	$\left.\begin{array}{l}C_{2n}H_{2n-1}O_2\\C_2H_3\end{array}\right\}$	$\left.\begin{array}{l}C_{2n}H_{2n-1}O_2\\Cl\end{array}\right\}$	$\left.\begin{array}{l}C_{2n}H_{2n-1}O_2\\C_{2n}H_{2n-1}O_2\end{array}\right\}$	$\left.\begin{array}{l}C_{2n}H_{2n-1}O_2\\H\end{array}\right\}O_2$	$\left.\begin{array}{l}C_{2n}H_{2n-1}O_2\\M\end{array}\right\}O_2$	$\left.\begin{array}{l}C_{2n}H_{2n-1}O_2\\C_{2n}H_{2n-1}O_2\end{array}\right\}O_2$	$\left.\begin{array}{l}C_{2n}H_{2n-1}O_2\\C_{2n}H_{2n-1}O_2\end{array}\right\}O_4$
Acetic. $\left.\begin{array}{l}C_4H_3O_2\\H\end{array}\right\}$	Acetone. $\left.\begin{array}{l}C_4H_3O_2\\C_2H_3\end{array}\right\}$	Acetic. $\left.\begin{array}{l}C_4H_3O_2\\Cl\end{array}\right\}$		Acetic. $\left.\begin{array}{l}C_4H_3O_2\\H\end{array}\right\}O_2$	Acetate. $\left.\begin{array}{l}C_4H_3O_2\\K\end{array}\right\}O_2$	Acetic. $\left.\begin{array}{l}C_4H_3O_2\\C_4H_3O_2\end{array}\right\}O_2$	Acetic. $\left.\begin{array}{l}C_4H_3O_2\\C_4H_3O_2\end{array}\right\}O_4$
Propionic. $\left.\begin{array}{l}C_6H_5O_2\\H\end{array}\right\}$	Propione. $\left.\begin{array}{l}C_6H_5O_2\\C_4H_5\end{array}\right\}$	Propionic. $\left.\begin{array}{l}C_6H_5O_2\\Cl\end{array}\right\}$		Propionic. $\left.\begin{array}{l}C_6H_5O_2\\H\end{array}\right\}O_2$	Propionate. $\left.\begin{array}{l}C_6H_5O_2\\K\end{array}\right\}O_2$	Propionic. $\left.\begin{array}{l}C_6H_5O_2\\C_6H_5O_2\end{array}\right\}O_2$	
Butyric. $\left.\begin{array}{l}C_8H_7O_2\\H\end{array}\right\}$	Butyrone. $\left.\begin{array}{l}C_8H_7O_2\\C_6H_7\end{array}\right\}$	Butyric. $\left.\begin{array}{l}C_8H_7O_2\\Cl\end{array}\right\}$	Butyryl. $\left.\begin{array}{l}C_8H_7O_2\\C_8H_7O_2\end{array}\right\}$	Butyric. $\left.\begin{array}{l}C_8H_7O_2\\H\end{array}\right\}O_2$	Butyrate. $\left.\begin{array}{l}C_8H_7O_2\\K\end{array}\right\}O_2$	Butyric. $\left.\begin{array}{l}C_8H_7O_2\\C_8H_7O_2\end{array}\right\}O_2$	

e and the organic peroxide may be thus exhibited in 's symbols :—

$$\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta}^{\text{Water.}} \;;\; \overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}\Theta_2}^{\text{Perox. of hydrogen.}} \;;\; \overbrace{\left.\begin{matrix}\text{Ȼ}_2H_3\Theta\\\text{Ȼ}_2H_3\Theta\end{matrix}\right\}\Theta}^{\text{Acetic anhydride.}} \;;\; \overbrace{\left.\begin{matrix}\text{Ȼ}_2H_3\Theta\\\text{Ȼ}_2H_3\Theta\end{matrix}\right\}\Theta_2}^{\text{Acetic peroxide.}}.$$

1) The table on the preceding page will assist in explaining tions of the principal classes of the derivatives of the ic acids.

§ III. THE FATTY ACIDS.

2) The fats and fixed oils when saponified yield a number , which belong to two different homologous series. Stearic lmitic acids may be taken as the types of one series, in he general formula of the normal acids is $(C_{2n}H_{2n})O_4$. The formula of the other series is $(C_{2n}H_{2n-2})O_4$; this series is nted by oleic acid, but only a few terms of it are known. oxidation of the members of these two groups a third f acids may be obtained, to which suberic and succinic elong: the acids of this group are dibasic: their normal s have the general formula $(C_{2n}H_{2n-2})O_8$. In the following he corresponding acids in each of these three groups are rated :—

ids of the form $C_{2n}H_{2n})O_4$, or $O,C_{2n}H_{2n-1}O_3$.	Acids of the form $(C_{2n}H_{2n-2})O_4$, or $HO,C_{2n}H_{2n-3}O_3$.	Acids of the form $(C_{2n}H_{2n-2})O_8$, or $2\,HO,C_{2n}H_{2n-4}O_6$.
ic . . $C_2H_2O_4$		
c . . $C_4H_4O_4$		Oxalic . . $C_4H_2O_8$
ionic . $C_6H_6O_4$	Acrylic . . $C_6H_4O_4$	Malonic . $C_6H_4O_8$
ric . . $C_8H_8O_4$		Succinic . $C_8H_6O_8$
ic . . $C_{10}H_{10}O_4$	Angelic . . $C_{10}H_8O_4$	Lipic . . $C_{10}H_8O_8$
ic . . $C_{12}H_{12}O_4$		Adipic . . $C_{12}H_{10}O_8$
nthylic $C_{14}H_{14}O_4$		Pimelic . . $C_{14}H_{12}O_8$
ylic . $C_{16}H_{16}O_4$		Suberic . . $C_{16}H_{14}O_8$
gonic . $C_{18}H_{18}O_4$		Anchoic . $C_{18}H_{16}O_8$
c . . $C_{20}H_{20}O_4$		Sebacic . . $C_{20}H_{18}O_8$
. . $C_{24}H_{24}O_4$		
tic . $C_{28}H_{28}O_4$		
tic . $C_{32}H_{32}O_4$	Physetoleic $C_{32}H_{30}O_4$	
c . . $C_{36}H_{36}O_4$	Oleic . . $C_{36}H_{34}O_4$	
fic . $C_{40}H_{40}O_4$		
c . . $C_{54}H_{54}O_4$		
ic . $C_{60}H_{60}O_4$		

s belonging to the Acetic or Stearic Series $(HO,C_{2n}H_{2n-1}O_3)$.

3) The acids which are comprised in this series constitute he most numerous and most carefully examined groups of

homologous compounds; all the terms of which, commencing with the formic and proceeding as far as the capric, are well known. The number of atoms of carbon in each of these terms is divisible by 2. It has been remarked, that in the terms which contain more carbon than the capric, the number of equivalents of carbon in all the acids which have been satisfactorily examined, is divisible by 4; although many chemists admit the existence of acids corresponding in composition to all the hydrocarbons divisible by 2, up to $(C_{40}H_{40})$. The fusing point of Brodie's cerotic acid is so much lower than that which might have been expected from an acid so high in the series, that Heintz has suggested that this exceptional case may possibly arise from the acid being a mixture of two others; since he finds it to be a general rule, that a mixture of any two of the solid acids of this series has a fusing point considerably below that of either of its components (1122), and the boiling point rises as the number for *n* increases. At the same time the acid property decreases excepting in particular cases: the lower terms generally displace those above them in the series from their combinations with bases; thus formic or acetic acid will displace the valeric.

The acids belonging to this group may all be distilled, either partially or completely, without undergoing decomposition. Many of them exhibit a remarkable peculiarity in the volume of vapour which they furnish at different temperatures; thus, the formic, the acetic, the butyric, and the valeric acids, at low temperatures, furnish a much smaller volume of vapour than they do at more elevated temperatures:—

	°F	Vapour density.
Formic acid at . .	51	3·23
Ditto . .	416	1·61
Acetic acid at . .	69	3·95
Ditto . .	320	2·48
Ditto . .	460	2·08
Butyric acid at . .	350	3·68
Ditto . .	502	3·07

At the higher temperatures, and at all points above them (until the acid undergoes decomposition), 1 equivalent of the compound yields 4 volumes of vapour; but at low temperatures the vapour volume does not correspond exactly to any specific multiple of the volume of oxygen.

All of the hydrated acids of this group when melted, with the exception of the formic and the acetic, exhibit the properties of ich is imperfectly soluble in water; though some of the nbers of the series are soluble in water to a considert: they are all abundantly soluble both in alcohol and

acids are regarded as monobasic, but several of them neutral and acid salts with the alkalies; a biformiate, te, and a bistearate of potash, for example, may be readily Many of them yield with oxide of lead, not only the nal salt, but also basic salts, which contain 3 equivalents f lead for each equivalent of acid. Many of these basic freely soluble in water.

emarkable relation which these acids bear to the alcohols ly been pointed out (p. 32);—for every alcohol there is nding acid, which may be formed from the alcohol by a process of oxidation: this oxidation may sometimes be lirectly—as in the conversion of wine alcohol into vinegar operation of finely divided platinum; but more usually essary to resort to indirect means, such as heating the ith hydrate of potash; in which case hydrogen is elimiilst oxygen enters into the compound, the general form uation being:—

$$H_{2n+1}O, HO + KO, HO = KO, C_{2n}H_{2n-1}O_3 + 2H_2.$$

action of gaseous chlorine upon the acids of this group to the formation of chlorinated acids, in which a certain of atoms of the hydrogen is displaced by an equal of equivalents of chlorine; but the saturating power of is not altered. In many cases more than one chlorinated be formed from the original acid; for example:—

id $HO,C_4H_3O_3$	Chloracetic acid . .	$HO,C_4\left.\begin{matrix}H_2\\Cl\end{matrix}\right\}O_3$
	Trichloracetic acid .	$HO,C_4Cl_3\ O_3$
. $HO,C_8H_7O_3$	Dichlorobutyric . .	$HO,C_8\left.\begin{matrix}H_5\\Cl_2\end{matrix}\right\}O_3$
	Tetrachlorobutyric .	$HO,C_8\left.\begin{matrix}H_3\\Cl_4\end{matrix}\right\}O_3$
. $HO,C_{10}H_9O_3$	Chlorovalerisic (Trichlorovaleric) .	$HO,C_{10}\left.\begin{matrix}H_6\\Cl_3\end{matrix}\right\}O_3$
	Chlorovalerosic (Tetrachlorovaleric)	$HO,C_{10}\left.\begin{matrix}H_5\\Cl_4\end{matrix}\right\}O_3$
. $HO,C_{36}H_{35}O_3$	Chlorostearic	$HO,C_{36}\left.\begin{matrix}H_{25}\\Cl_{10}\end{matrix}\right\}O_3$

Several of these acids also furnish nitro-acids, when with fuming nitric acid; such, for example, as the following:—

Nitropropionic acid . .	$HO, C_6\,H_4NO_4, O_3$
Nitrobutyric acid . .	$HO, C_8\,H_6NO_4, O_3$
Nitrovaleric acid . .	$HO, C_{10}H_8NO_4, O_3$.

An interesting observation was made by Kolbe regarding th mode in which the salts of these acids are decomposed by voltaic battery. The first stage of the electrolysis consists in th separation of the salt into two portions; the metal going to negative plate, whilst the acid and the oxygen travel towards th positive electrode. Here the second stage of the process co mences; the oxygen and the acid, reacting upon each other definite manner. When, for example, a strong solution of vale of potash is submitted to the action of four cells of Bunsen's of Grove's battery, the temperature of the solution being p vented from rising much beyond 32° F., the potassium of the is evolved as usual at the negative electrode; and by here deco posing an equivalent of water it immediately forms potash, liberates an equivalent of hydrogen: but instead of pure val acid being liberated at the positive plate, carbonic acid an quantity of an ethereal oil, with a portion of undecomposed val acid, are set free. This ethereal oil consists chiefly of tetryl, butyl $(C_8H_9)_2$, the radicle of the fourth alcohol. No oxy escapes; the valeric acid having undergone oxidation in the m ner indicated by the following symbols:—

$$2\,(\overbrace{KO,C_{10}H_9O_3}^{\text{Valerate of potash.}})\text{ yields }\overbrace{K_2}^{\overset{\text{Cathion.}}{+}};\ 2\,\overbrace{C_{10}H_9O_4}^{\overset{\text{Anion.}}{-}}:\text{ and }K_2+2\,H_2O_2\text{ beco}$$

$$2\,(KO,HO)+H_2;\text{ whilst }2\,C_{10}H_9O_4\text{ breaks up into }(\overbrace{C_8H_9}^{\text{Tetryl.}})_2+\overbrace{2\,C}^{\text{Carb}}$$

Other salts of the same class of acids present analogous nomena: the acetates yield methyl: the butyrates, trityl (prop and, generally, it is found that on decomposing the salts of stearic group by the voltaic current, they yield at the posi electrode, carbonic acid and the radicle of the alcohol immedia below them in the series. Hence, Kolbe was led to regard acids of this group as coupled oxalic acids; each acid contain the radicle of the particular alcohol which is separated duri electrolysis; for instance:—

	Kolbe.		Gerhardt.
Acetic acid	= $HO,(C_2H_3)C_2O_3$	or Methyl-formic	$HO,C_2(C_2H_3)O_3$
Propionic	= $HO,(C_4H_5)C_2O_3$	or Ethyl-formic	$HO,C_2(C_4H_5)O_3$
Butyric	= $HO,(C_6H_7)C_2O_3$	or Trityl-formic	$HO,C_2(C_6H_7)O_3$
Valeric	= $HO,(C_8H_9)C_2O_3$	or Tetryl-formic	$HO,C_2(C_8H_9)O_3$;

and so on. Gerhardt prefers to regard them as derivatives of formic acid, in which the hydrogen of the formic acid is displaced by the radicles of the alcohols: this view accords equally well with the results of electrolysis, and is certainly more in harmony with the present state of our knowledge of the mode in which chemical compounds are formed. Such a supposition, however, does not indicate any theory as to the molecular constitution of formic acid; it merely states that in whatever way formic acid be constituted, the higher acids of the group are probably similar in their atomic arrangement: formic acid might therefore possibly be an oxide of a radicle which itself contains oxygen:—

Formic acid would then be . $HO, [C_2(H)O_2]O$
Acetic acid ,, . $HO, [C_2(C_2H_3)O_2]O$
Propionic acid ,, . $HO, [C_2(C_4H_5)O_2]O$.

Some difficulty is experienced in procuring the soluble salts of the higher fatty acids in a state of purity, since few of them crystallize readily from their aqueous solutions. The baryta salts when soluble, however, generally admit of being procured in well-defined forms. The solubility of the baryta salts decreases as the number of atoms of carbon in the acid increases.

The soda salts of this group of acids are all soluble in hot water, and are therefore easily prepared by boiling the fatty acid with a slight excess of the alkali. This excess of alkali may be removed from the soda salts of the higher terms of the series, by taking advantage of their insolubility in a concentrated solution of chloride of sodium; for as soon as the solution of the soap is poured into strong brine, the soda soap is separated in the form of a curdled granular mass, which can be easily collected on a linen filter and pressed, whilst the excess of soda remains in solution with the chloride of sodium. The coagulated soap is then to be re-dissolved in water, and salted out once or twice more: finally, the soda salt may be purified from the chloride of sodium by re-crystallization from alcohol.

The foregoing process cannot be adopted with the potash salts, since the potash soaps are decomposed when mixed with chloride of sodium, a soda soap being formed whilst chloride of potassium remains in solution. Chloride of potassium cannot be substituted

for chloride of sodium in salting out, since the soaps a
soluble in a solution of chloride of potassium. The me
used in the preparation of the pure potash salts consists,
—in boiling the acid with an excess of carbonate of pot
rating the solution to dryness, and then separating the
from the excess of carbonate by dissolving the soap in al
evaporation of the alcoholic solution, the potash salt
acid may generally be obtained in crystals.

The insoluble soaps may be procured by double deco
a pure and rather dilute solution of the potash or of th
being mixed with a dilute solution of a salt of the met
such as sulphate of copper, acetate of lead, or nitrate
according as a compound of copper, of lead, or of silver,

The following table indicates the composition of t
the acetic series, and the melting point of each acid
source whence it is obtained :—

Acids.	Formulæ.	Melting point ° F.	Boiling point ° F.	Whence ob
Formic . .	$HO,C_2\,H\;\,O_3$	21	221	Red ants; di oxalic acid; tion of amy other organi
Acetic . .	$HO,C_4\,H_3\,O_3$	63	243	Distillation wood; oxid of alcohol, &
Propionic .	$HO,C_6\,H_5\,O_3$		284	Fermentatio glycerin, &c
Butyric .	$HO,C_8\,H_7\,O_3$	below °	314	Butter; fer tation of acid, &c.
Valeric . .	$HO,C_{10}H_9\,O_3$	below °	347	Valerian oxidation o sel oil.
Caproic .	$HO,C_{12}H_{11}O_3$		392	Butter.
Œnanthylic	$HO,C_{14}H_{13}O_3$	below °	298?	Castor oil by tillation, &c
Caprylic .	$HO,C_{16}H_{15}O_3$	59	457	Butter; cocoa-n
Pelargonic.	$HO,C_{18}H_{17}O_3$		500	Leaves of th ranium.
Capric . .	$HO,C_{20}H_{19}O_3$	86		Butter; oil oxidation.
Lauric . .	$HO,C_{24}H_{23}O_3$	110		Cocoa-nut oi the bay tre
Myristic .	$HO,C_{28}H_{27}O_3$	129		Nutmeg but nut oil, &c
Palmitic .	$HO,C_{32}H_{31}O_3$	143·6		Palm oil; wax, &c.
Stearic . .	$HO,C_{36}H_{35}O_3$	159		Most solid a
Arachidic .	$HO,C_{40}H_{39}O_3$	167		Butter; oil o
Cerotic . .	$HO,C_{54}H_{53}O_3$	174		Bees' wax.
Melissic .	$HO,C_{60}H_{59}O_3$	192		Bees' wax.

(1104) **Formic Acid** ($HO,C_2HO_3=9+37$). *Sp. gr. of liquid* 1·2227 *at* 32°; *of vapour* 2·125.—This acid derives its name from the circumstance of its having been first obtained from the *Formica rufa*, or red ant, which when irritated ejects a concentrated acid liquid, which produces a stinging sensation when applied to the skin: the same acid is excreted by several other insects. It is also found in a free state in the leaves of the stinging-nettle (*urtica urens*). Formic acid, however, derives its importance from the variety of chemical reactions by which it is produced. It is a frequent product of the oxidation of organic bodies; those which belong to the amylaceous group yield it by various processes of oxidation; such as by heating them with hydrate of potash, or with chromic acid, or with a mixture of sulphuric acid and peroxide of manganese. When grape sugar is triturated with peroxide of lead, water is eliminated, and a mixture of carbonate and formiate of lead is produced. Gelatin and the albuminoid bodies also yield it, mixed with a variety of other products, when they are submitted to the oxidizing influence of chromic acid, or of a mixture of sulphuric acid and black oxide of manganese.

Preparation.—The preparation of formic acid may be effected in the laboratory in several ways.

1. Berthelot has recently established the important fact of the synthesis of formic acid by acting upon moist hydrate of potash by means of carbonic oxide: the gas becomes slowly absorbed when exposed in contact with the moistened alkali to a temperature of 212°:—

$$KO,HO+C_2O_2=KO,C_2HO_3.$$

The quantity of the acid obtained in this remarkable reaction is too small to furnish an available source of the acid.

2. Oxalic acid, when mixed with an equal bulk of sand, and distilled, may also be employed as a source of formic acid, whilst carbonic acid is expelled:—

$$\overbrace{2\ HO,C_4O_6}^{\text{Oxalic acid.}} = \overbrace{HO,C_2HO_3}^{\text{Formic acid.}}+C_2O_4.$$

In the ordinary mode of conducting this operation a large quantity of the formic acid is itself decomposed, owing to the high temperature required to effect the distillation; water and carbonic oxide being the result of its decomposition:—

$$HO,C_2HO_3=H_2O_2+C_2O_2.$$

Berthelot has, however, succeeded in rendering this decomposition perfectly manageable in the following manner:—

2 lb. of syrupy glycerin, and 4 or 5 ounces of water, are placed in a retort into which 2 lb. of commercial oxalic acid have been introduced: a receiver is then adapted to the retort, and the temperature is gradually raised to 212° or 220°. Brisk effervescence soon ensues owing to the escape of pure carbonic acid: in about fifteen hours the whole of the oxalic acid is decomposed; a small quantity of formic acid will be found condensed in the receiver, but the greater portion remains in the retort. A pint of water is next added to the contents of the retort, and the solution is distilled, adding fresh water as fast as it evaporates. When a gallon and a half or two gallons of water have thus been distilled, the whole of the formic acid will have passed over. The glycerin which remains in the retort may be employed as before to decompose a fresh portion of oxalic acid, and the same series of operations may be repeated with the same quantity of glycerin for an indefinite number of times. Crystallized oxalic acid thus furnishes more than a third of its weight of monohydrated formic acid. This is the best and most productive process at present known for the preparation of formic acid. The principal precaution required is not to allow the temperature to rise too high: if it reach 360° or 390° the formic acid itself is decomposed, and an evolution of pure carbonic oxide takes place. This reaction may be taken advantage of in order to obtain pure oxide of carbon by means of oxalic acid. The glycerin acts in some manner unknown in favouring the decomposition of oxalic acid at a lower temperature than would occur if heat alone were employed to effect the metamorphosis: no chemical action, so far as is yet ascertained, takes places between the glycerin and any of the compounds concerned in the reaction (*Ann. de Chimie,* III. xlvi. 484). A solution of mannite acts upon oxalic acid at 212°, in a manner similar to one of glycerin.

3. Formic acid may also be obtained by the oxidation of methylic alcohol under the influence of finely divided platinum:—

$$\overbrace{C_2H_4O_2}^{\text{Wood spirit.}} + O_4 = \overbrace{HO,C_2HO_3}^{\text{Formic acid.}} + H_2O_2.$$

The oxidation, however, is very liable to proceed too far, water and carbonic acid being formed in large quantity:—

$$2\,(HO,C_2HO_3) + O_4 = 2\,C_2O_4 + 2\,H_2O_2.$$

4. The method which has generally been resorted to for the preparation of formic acid, is one discovered by Döbereiner, and modified by Liebig. This consists in mixing in a very capacious

ts of deutoxide of manganese, and 4 ric acid are then added by degrees, up to 8 or 10 times its bulk, from the rbonic acid. When this has ceased, with, and an impure, dilute formic acid tralized by carbonate of lead, and the crystallization. When this salt is distilled of sulphuric acid, the pure monohydrated ver.

onohydrated formic acid is a fuming liquid of It is extremely corrosive, and occasions vesiful sores if dropped upon the skin. Below 32° it brilliant scales, and boils at 221°·5, yielding an pour which burns with a blue flame. Formic acid definite hydrates with water, HO,C_2HO_3, and HO,

dt was unsuccessful in his attempts to procure the of formic acid.

ates.—Formic acid is considered to be monobasic, but of potash and soda may be obtained. All the formiates le. *Formiate of soda* ($NaO,C_2HO_3 + 2\,Aq$) assumes the rhombic prisms, which are slightly deliquescent. *Forbaryta* crystallizes readily in brilliant anhydrous prisms. *of lead* requires about 40 parts of cold water for solut it is freely soluble in hot water, from which it crystallong prismatic anhydrous needles. If a current of sulphuydrogen be passed over this salt, while it is gently heated g tube, sulphide of lead is formed, and a monohydrate of is liberated, and may be collected in a suitable receiver. A *tribasic formiate of lead* may also be obtained. *Formiate r* ($CuO,C_2HO_3 + 4\,Aq$) crystallizes in large blue rhomboidal it forms double salts with the formiates of baryta and

nic acid is easily reconverted into oxalic acid. If a mixrmiate of soda and hydrate of baryta be heated, hydrogen d, and an oxalate of one of the bases is formed; 2 atoms c acid containing the elements of 1 atom of oxalic acid, oms of hydrogen :—

$$\overbrace{2\,(HO,C_2HO_3)}^{\text{Formic acid.}} = \overbrace{2\,HO,C_4O_6}^{\text{Oxalic acid.}} + H_2.$$

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substances, *such as sugar, chaff,* bran, sawdust, tartaric acid, *tuted for starch in this operation* with more or less effect.

By a stronger heat the oxalic acid is decomposed, and c acid is formed. Chlorine converts formic acid entirely into chloric and carbonic acids. Nitric acid and other oxidizing convert it into carbonic acid and water. Formic acid is a p reducing agent, the free acid at a boiling temperature redu salts of silver, of mercury, of gold, and of platinum, whil carbonic acid is evolved. Its reducing action upon the con of platinum may sometimes serve as an indication of the p of formic acid in solution. The formiates are decomp strong sulphuric acid in excess, pure carbonic oxide an being the sole products; $HO,C_2HO_3=C_2O_2+H_2O_2$.

(1105) 2. ACETIC ACID ($HO,C_4H_3O_3=9+51$).—Th was one of the earliest known of the organic acids, and of the most important. In a dilute form, mixed with impurities of vegetable origin, it constitutes ordinary which rarely contains more than 5 per cent. of the an acid.

Preparation.—The existence of acetic acid in the j plants has not been satisfactorily proved, but it is forme cially in a variety of processes.

1. A large quantity is furnished during the destruc tillation of wood in iron retorts by means of a heat g raised to low redness. The wood is usually placed in these in loose iron cases, by which means the charge can be introduced without loss, while the retort is still hot, charcoal can be withdrawn when the distillation is comple harder kinds of wood, particularly the oak, beech, birch, are those which yield it most abundantly, the quantity varying from 1½ to 3½ per cent.; the crude acid thus ob called in the arts, *pyroligneous acid*. A large quantity matter comes over during the operation, accompanied volatile and inflammable bodies, among which wood-spirit, of methyl, and acetone predominate. These bodies are co in suitable receivers, whilst in addition to carbonic acid siderable quantity of combustible gases, composed ch hydrogen and carbonic oxide, are directed into the furnac they serve as fuel, and aid in heating the retorts. In a hours, or as soon as the gases cease to escape, the lo cylinders containing the wood are withdrawn, and imm closed with an air-tight cover, so as to allow the charcoal excluded from the atmosphere. The crude acid liquid wh been collected in the condenser is decanted from the

submitted to distillation, furnishes *wood naphtha,* which
itutes the more volatile portions; afterwards the acetic acid
llected; the latter, however, is always accompanied by tarry
ers. In order to get rid of these, the liquid is neutralized by
ddition of milk of lime, or of carbonate of soda; a quantity
r rises to the surface of the liquid; on standing, this is skim-
off, and the solution of crude acetate thus obtained is evapo-
, and the dry residue, if soda be used, cautiously roasted at a
rature of about 500° to expel the tarry matters. It is after-
redissolved in water, decanted from the carbonaceous par-
which are allowed to subside; then recrystallized, and sub-
d to distillation with sulphuric or with hydrochloric acid,
lphuric being preferable when acetate of soda is employed,
hydrochloric acid answers best when acetate of lime is
The greater part of the acetic acid consumed in the arts in
ountry is obtained by this method. The black acetate of
btained by saturating the crude pyroligneous acid after the
lized solution has been boiled with a small quantity of sul-
of lead in order to remove colouring matter, is also exten-
ly employed in preparing *red liquor,* a rough acetate of alumina
d by the calico-printer for fixing the red dye of madder upon
cloth.

Mollerat, taking advantage of the insolubility of sulphate
oda in acetic acid, obtains a nearly pure acid at once, by
ing sulphuric acid to flow into a deep vessel containing a
entrated solution of the acetate of soda, in the proportion of
or 36lb. of oil of vitriol for every 100lb. of acetate of soda.
sulphuric acid is caused to flow quietly under the salt without
ing with it, in order that the heat developed by the reaction
be very moderate; the materials are then slowly mixed, and
r standing for a few hours the decomposition is complete; the
nts of the vessels gradually separate into two layers, the
one containing the concentrated acetic acid, and the lower
consisting of sulphate of soda. The acetic acid is drawn off
a syphon, and is afterwards rendered pure by distillation.
last traces of empyreumatic matter may be got rid of by
ication from a small quantity of bichromate of potash.

In countries where alcohol is cheap, and particularly in
many, dilute acetic acid is prepared on a large scale by the
ation of alcohol in the manner already described (1078), the
ted spirit being made to trickle slowly over a large surface of
shavings contained in vats of *suitable construction.*

(1105) 3. *Vinegar.—The vinegar which is* most esteemed for

culinary purposes is that prepared from wine; it is
manufactured in France, from the acescent varieties of w
wine is introduced into large casks capable of containing
gallons each; they are arranged in rows in a shed, th
ture of which is kept at from 75° to 85°. The upp
these casks is partially open to allow the access of air.
quantity of good vinegar at a boiling temperature is t
in each cask, and every eight days a few gallons of fres
added until the casks are about two-thirds full. In ab
night from this time, the acidification is complete: a f
of the vinegar are then drawn off from each cask, and t
are again filled up to the same extent with a fresh quan
wine to be acidified. It is found that the acetification t
much less rapidly in new casks than in those which have
for this purpose for some time. In the old casks a qu
gelatinous conferva becomes developed, and this substa
has received the name of *mother of vinegar*, favours the
of oxygen by the alcohol, in a manner which is supp
somewhat analogous to that in which platinum black
similar circumstances (859).

The following method of preparing vinegar, contrive
haave, is still practised extensively:—Two large vats are
vided with a false bottom supported at a height of ab
above the floor of the vessel. Each vat is filled with vin
and *rapes*, or the footstalks and skins of grapes; the vat
charged with wine, one of them being completely filled,
other only half filled. In this state the two vessels a
twenty-four hours at a temperature of 75°. At the exp
this time the vat which had been left only half full is fille
the full one, and thus every twenty-four hours a portio
wine is transferred alternately from one vat to the oth
acetification goes on most rapidly in the vat which is
full, and in this a sensible elevation of temperature ma
ceived after the first three or four days, but it shou
allowed to rise beyond 80°. The process requires from a
to three weeks for its completion, according to the temp
the atmosphere at the time. The vinegar is finally draw
settling casks, and when clear is fit for use.

4. Infusion of malt, weak solutions of sugar, and
tures of starch with yeast, furnish very good vinegar. Mal
is the principal variety of vinegar employed for domestic
in England. According to Ure, a good vinegar for dom
poses may be prepared by adding to each gallon

of 1¼lb. of sugar and 1 gallon of water, a quarter of a
ast. If kept for three days at a temperature of 75° or
ll be sufficiently acidified to allow of being drawn off
ripening cask, where 1 ounce of bruised raisins and 1
crude tartar are to be added to each gallon of liquor.
sweet taste has quite disappeared, it should be drawn off
s and corked down tightly; it is stated that such vinegar
in 5 per cent. of pure acetic acid. In all cases where
formed by the oxidation of alcohol, it is necessary to
absorption of oxygen and the process of acetification, by
ce of yeast, or of some albuminous matter such as is
contained in solution in the juices of plants or in vege-
sions made at ordinary temperatures. A pure dilute
f alcohol is not susceptible of acidification by exposure to

ar prepared by the foregoing methods from fermented or
le liquors contains a large quantity of foreign matters,
ly all of which it may be freed by simple distillation:
iquid which comes over constitutes what is known in
as *distilled* vinegar. The strength of any vinegar is best
d by determining the quantity of anhydrous carbonate
hich a given weight of it will neutralize: 100 grains of
of soda corresponding to 96·2 grains of the anhydrous
re must be taken to ascertain the absence of sulphuric
y other acid except the acetic, when operating in this
ommercial vinegar is allowed by law to contain $\frac{1}{1000}$th of
of sulphuric acid; the presence of which prevent the
rom becoming mouldy.

hydrated acetic acid is best procured in a pure form by
82 parts, or 1 equivalent, of fused acetate of soda, with 98
2 equivalents, of oil of vitriol, at a gentle heat, and recti-
product from a small quantity of bichromate of potash.
tate of lead may be substituted for the soda salt, but
re than 1 equivalent of the salt must be taken for each
t of oil of vitriol, and the mixture must be digested for
before distilling. Either binacetate of potash or acetate
, when submitted to distillation without any addition, also
the concentrated acid with facility; but when prepared
anner it is liable to be contaminated with acetone.

7) *Properties of Acetic Acid.*—Normal acetic acid (HO,
Sp. gr. 1·063 at 63°) is liquid at temperatures above 63° F.,
oint it crystallizes in *radiating tufts of plates.* It may
in all *proportions with water,* and its density increases

on dilution, until nearly one-third of its weight of water
added, when it contains ($HO,C_4H_3O_3+2\,Aq$) with a
1·079. If it be further diluted, the density diminishes
to the ordinary law. In consequence of this anomaly,
drated acetic acid, and the same acid diluted with an eq
of water, possess each the sp. gr. 1·063. The concent
has a sharp aromatic taste, and a peculiar pungent
blisters the skin if applied to it for a sufficient length of
boils at 243°, and may be distilled unchanged. The
this acid is inflammable, producing by its combustion
carbonic acid. The vapour of acetic acid exhibits an
dilatation when exposed to a gradually rising temperatur

At 69°	the density is	3·95	At 392°	the density i		
At 257°	,, ,,	3·2	At 446°	,,	,,	
At 320°	,, ,,	2·48	At 460°	,,	,,	

and beyond this it undergoes no further alteration unti
is itself decomposed. At 446° and upwards, 1 atom o
follows the usual law of yielding 4 volumes of vapour (B

(1108) *Acetic anhydride* ($C_4H_3O_3, C_4H_3O_3$) : *Sp. gr.*
at 69°, 1·073 ; *of vapour* 3·47 ; *Boiling pt.* 279°·5.—This
was obtained by Gerhardt by several methods; but t
consists in distilling 3 parts of oxychloride of phosph
6½ of anhydrous acetate of soda, returning the liquid wh
over, upon the residue, and redistilling, until the odo
chloride has disappeared; finally the liquid is rectified.
colourless, very mobile liquid of high refracting power ; w
pungent smell, resembling that of acetic acid, combined
of the hawthorn blossom. It emits a vapour which is
irritating to the eyes. Acetic anhydride does not mix im
with water, but sinks through it in oily drops, whic
slowly dissolved, evolving heat, and forming the ordinary
acid. This anhydride gradually absorbs moisture from
and becomes converted into hydrated acetic acid. Potas
rapidly upon it, an inflammable gas being given off, and
pound being by degrees converted into a crystalline mass
drous binacetate of potash ($KO, 2\,C_4H_3O_3$). The same
is also formed by dissolving dried acetate of potash in
dride.

(1109) *Acetates.*—Acetic acid is monobasic. M
are largely used in the arts. *Acetate of Potash* (K
which is employed medicinally as a diuretic, is

d, very deliquescent, fusible salt, abundantly soluble in
l. It combines with a second equivalent of acetic acid when
ed in the concentrated acid, and forms a crystallizable bin-
e, which when subjected to distillation is decomposed into
monohydrated acetic acid and normal acetate of potash.
f Soda ($NaO,C_4H_3O_3+6\ Aq=82+54$) crystallizes in
rhombic prisms: it fuses readily. This salt is prepared
ge quantities during the purification of wood-vinegar, the
acid being neutralized sometimes directly by means of car-
of soda, or soda ash; but in many manufactories, after the
acid has been neutralized by chalk and thus converted into
of lime, the liquid is mixed with sulphate of soda in the
tion of two equivalents of the sulphate to one of the acetate.
ble acetate of soda is thus obtained by double decomposition,
a heavy crystalline double sulphate of lime and soda is
which can be more easily freed from the mother liquor
e pasty mass which the simple sulphate of lime would pro-
Acetate of Ammonia is a very soluble salt, which is fre-
y used medicinally as a diaphoretic. *Acetate of Baryta*
lles below 60° with 3 Aq, in oblique rhombic prisms; at
emperatures its crystals assume the form of flattened
and retain only 1 Aq: it is more soluble in cold than in
er, and is slightly soluble in alcohol; it is occasionally
precipitant for sulphuric acid; when distilled it furnishes
Acetate of Lime ($CaO,C_4H_3O_3=79$) crystallizes in silky,
ous needles, which are very soluble in water: if heated to
becomes strongly phosphorescent by gentle friction.

etates of Alumina.—These compounds are extensively manu-
d for the use of the dyer and calico-printer. The common
dant is prepared by precipitating 100 parts of alum in
n by means of 120 of crystallized acetate of lead: the sul-
potash of the alum remains undecomposed in the solution.
es sulphate of alumina is used instead of alum. Crude
of lime is also extensively substituted for acetate of lead in
eration. Sulphate of lime is precipitated and acetate of
remains in solution. When this liquor is used as a mor-
is thickened with gum, and applied by means of blocks to
th. The acetates of alumina have been carefully studied by
who has obtained several new and important results (*Q. J.
Soc.* vi. 216). He has proved the existence of two insoluble
ates of alumina ($Al_2O_3, 2\ C_4H_3O_3 + 5\ Aq$), and ($Al_2O_3$,
$O_3 + 2\ Aq$), besides a soluble *binacetate* ($Al_2O_3, 2\ C_4H_3O_3$
The *easiest method of preparing the* commercial acetate

of alumina consists in decomposing a solution of tersulph alumina with one of acetate of lead; but although 3 equivale sulphuric acid are thus removed, and 3 equivalents of acetic ac liberated, no solid teracetate of alumina can be obtained fro liquid. Indeed Crum is of opinion that, even when in sol the salt which is thus formed is a binacetate of alumina, mixed an equivalent of free acetic acid, since the liquid has a pu ful odour of acetic acid; $Al_2O_3, 3\,SO_3 + 3\,(PbO,C_4H_3O_3)$ $=3\,(PbO,SO_3) + Al_2O_3, 2\,C_4H_3O_3 + HO,C_4H_3O_3$.

If a concentrated solution, containing from 4 to 5 per ce alumina, prepared in the manner just directed, in such a proportions as to contain a teracetate of alumina, be purified traces of lead by sulphuretted hydrogen, and from those o phuric acid by acetate of baryta, a liquid is obtained which, kept at between 60° and 70° F. for a few days, gradually dep white coating upon the sides of the vessel; this deposit, when al to become dry spontaneously, forms white hard plates rese porcelain in appearance. This is a binacetate of alumina ($2\,C_4H_3O_3 + 5$ Aq), which is insoluble in water, but solu nitric acid. If the original solution of the teracetate of al be boiled, a heavy white powder is rapidly deposited, and th tion retains scarcely a trace of alumina: Crum found this p tate to be a different hydrate of the binacetate of alumina ($2\,C_4H_3O_3 + 2$ Aq). When dilute solutions of the acet alumina are employed, no precipitate is occasioned unless siderable excess of free acetic acid be added. When the s of the teracetate is evaporated rapidly by spreading it in thin films over a sheet of glass, the heat not being allowed above 100° F., and the oily drops as they run together bei stantly spread out with a thin platinum knife, a dry substan be obtained in transparent scales ($Al_2O_3, 2\,C_4H_3O_3 + 4$ Aq), may be redissolved easily and completely in water.*

Many other acetates are also used as mordants in

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* From this compound, the remarkable soluble hydrate of alu viously alluded to (565), may be prepared in the following man dilute solution of this soluble binacetate of alumina, contain of its weight of alumina, be placed in a closed vessel which is im water, maintained at the boiling point, for about ten days, the solu dually loses its astringent taste, and acquires a strong odour of If this liquid be now diluted with rather more than an equal bulk and be boiled briskly in a shallow dish, the layer of liquid not than a quarter of an inch in depth, and water being supplied in pr it evaporates, the acetic acid may in about an hour and a half be dr as to be no longer sensible to litmus paper. The liquid remains transparent, but is quite tasteless. When 1 grain of sulphuric

ng; for example, those of *manganese*, *zinc* ($ZnO,C_4H_3O_3$
Aq) and *iron*. Acetic acid dissolves iron readily with evolu-
of hydrogen; the crude acetate of iron, prepared by dissolving
hoops in raw wood-vinegar, is employed for preserving wood
cherie's process (960). The *protacetate of iron* crystallizes in
needles, which rapidly absorb oxygen. The *peracetate of*
is of a deep red colour.

cetates of Lead.—Acetic acid forms several compounds with
of lead—viz., the

Neutral acetate . .	$PbO, \ C_4H_3O_3+3\ Aq,$
Subsesquiacetate . .	$3\ PbO, 2\ C_4H_3O_3+\ Aq,$
Tribasic acetate . .	$3\ PbO, \ C_4H_3O_3+\ Aq,$
Hexacetate	$6\ PbO, \ C_4H_3O_3+\ Aq.$

eutral acetate and the tribasic acetate are important salts.
he *neutral acetate of lead* ($PbO,C_4H_3O_3+3\ Aq=162{\cdot}6+27$)
e procured by dissolving litharge in excess of acetic acid: by
ating the solution, the salt may be obtained crystallized in
rhombic prisms, which are sometimes opaque, but generally
arent: its more usual form, however, is that of a mass of con-
minute white crystals, much resembling loaf sugar; it also
sweetish metallic taste, and from this circumstance it derives
mmon name of *sugar of lead*: when exposed to the air it is
scent. It is soluble in less than twice its weight of water,
also freely soluble in alcohol. When heated it first becomes
rous, and then fuses to a clear liquid. If the heat be raised

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f water is mixed with 8000 grains of such a solution (a quantity which
20 grains of alumina), the whole is converted into a solid, transparent
y pressure in a bag the volume of this jelly may be reduced to one-
of its original bulk, the solid coagulum retaining nearly the whole of
aric acid, which amounts to about 1 equivalent of the acid to 15 of
One atom of the tribasic citric acid produces as powerful an effect
lating the solution as 3 equivalents of sulphuric acid, and 1 atom of
acid as much as 2 equivalents of sulphuric acid, but of hydrochloric
c acids not less than 300 equivalents are required to produce an effect
ation equal to that occasioned by 1 equivalent of sulphuric acid. One
otash dissolved in 1000 of water coagulates 9000 grains of the solu-
d soda, ammonia, and lime have an equally powerful effect. An excess
as well as of sulphuric or hydrochloric acid, dissolves the coagu-
erting the alumina into its ordinary modification. Solutions of the
coagulate the solution as readily as free sulphuric acid.
na, in this soluble condition, has lost its power of acting as a mordant.
the precipitated binacetate of alumina is kept for an hour or two
of boiling water with constant agitation, it becomes gradually
d may then by digestion be converted into free acetic acid,
e hydrate of alumina. *The soluble hydrate of alumina, when
112°, retains 2 equivalents of water.*

further, acetone, $C_6H_6O_2$, is formed, carbonic acid escapes,
mass becomes solid. In this state it consists of *subsesqui*
lead (3 PbO, 2 $C_4H_3O_3$ + Aq); this salt is readily soluble
alcohol and in water; it has a distinctly alkaline reaction,
tallizes in pearly scales: the same salt may also be fo
adding the neutral acetate in the proportion of 19 parts, o
to 39½, or 1 atom of a concentrated boiling solution of th
acetate of lead.

Triacetate of lead (3 PbO,$C_4H_3O_3$ + HO), commonly
Goulard's Extract, is prepared by digesting 7 parts of fi
dered litharge with 6 parts of acetate of lead, dissolved in
of water: it has a strongly alkaline reaction. The s
the oxide of lead is effected much more rapidly if
basin be used than if one of glass or porcelain be
The salt crystallizes in opaque needles. Payen obtai
salt in well-formed crystals, by adding a solution of
to a hot solution of 1 part of the neutral acetate in
water. Tribasic acetate of lead is insoluble in alcohol. Pa
in its aqueous solution and dried, burns like tinder whe
Solutions both of this and of the preceding salt are d
by carbonic acid; neutral acetate of lead is left in the li
hydrated oxycarbonate of lead is precipitated in silky, w
luble crystals. This fact forms the basis of the method
paring white lead (768).

Acetates of Copper.—Four of these compounds m
tained, viz.:—

Neutral acetate, or verditer	CuO, $C_4H_3O_3$ +
Subsesquiacetate . . .	3 CuO, 2 $C_4H_3O_3$ +
Diacetate, or verdigris . .	2 CuO, $C_4H_3O_3$ +
Tribasic acetate . . .	3 CuO, $C_4H_3O_3$ + 1

Neutral acetate of copper (CuO,$C_4H_3O_3$ + Aq = 90·7 +
commerce under the name of *verditer*. It is prepared
a solution of 1 equivalent of sulphate of copper with an
of acetate of lead, also in solution, and evaporating the
decanted from the sulphate of lead; it yields obliqu
prisms of a fine green colour. By exposure to the air,
of the acid escapes, and the crystals become cover
efflorescence composed of dibasic acetate of copper. If th
crystallized from an acid solution below 40°, a blue salt
with 5 equivalents of water.

The *diacetate of copper*, or *verdigris* (2 CuO,C_4H_3
is prepared for commercial purposes by piling up sheet

lternate layers of the fermenting husks of raisins: after
of some weeks the plates of copper become covered with
of the salt; this is detached, made into a thick paste with
r, and pressed into moulds. The mass thus obtained is of
h green colour, it is tough and is reduced to powder with
ty. In this mode of preparing the salt, the alcohol con-
in the grape skins becomes slowly oxidized and converted
etic acid; the metal also absorbs oxygen gradually from
; and the oxide thus formed combines with the acetic

rdigris, when treated with water, is decomposed into an
le tribasic acetate of copper, and a soluble *subsesquiacetate*
, $2\,C_4H_3O_3+6\,Aq$): the latter salt may be obtained in
on evaporating the solution.

tribasic acetate ($3\,CuO,C_4H_3O_3+1\frac{1}{2}\,Aq$) is the most stable
acetates of copper; it assumes the form either of bluish
edles, or of a green crystalline powder: when heated to
becomes anhydrous.

e neutral acetate of copper unites with the arsenite of this
forming *Schweinfurt green*, $CuO,C_4H_3O_3+3\,(CuO,AsO_3)$.
be obtained by mingling boiling solutions of equal weights
nious acid and acetate of copper, and adding to the mixture
al bulk of cold water: if it be allowed to stand for some
beautiful crystalline green pigment is produced.

bacetate of mercury ($Hg_2O,C_4H_3O_3$) is the least soluble
acetates; it is dissolved readily by boiling water, but it is
ly decomposed by ebullition of the solution, and converted
mixture of metallic mercury and a sparingly soluble basic
. The subacetate crystallizes in silvery scales, which are
y blackened by exposure to light.

etate of silver ($AgO,C_4H_3O_3,=167$) is occasionally employed
agent; it is sparingly soluble in cold water, but is readily
ed by hot water, which on cooling deposits it in thin,
, anhydrous, silky needles. It is readily obtained by mix-
oncentrated solution of nitrate of silver with a solution of
of potash, or acetate of soda.

e acetates are distinguished by the pungent odour of acetic
hich they emit when heated with sulphuric acid. When
with lime they yield acetone (1087), which has a peculiar
aracteristic odour; when distilled with hydrate of potash
ield light carburetted hydrogen; and upon this reaction the
ethod of obtaining marsh gas is *founded* (401).

d solutions *of the acetates give with nitrate* of suboxide of mercury, a precipitate of the subacetate. Another character is the formation with oxide of lead of a soluble basic salt, with an alkaline reaction.

Some of the acetates, as those of baryta and strontia, form double salts with the nitrates of these bases when equivalent quantities of the two salts are dissolved in water and allowed to evaporate spontaneously; the strontia salt contains $SrO,C_4H_3O_3+SrO,NO_5+3\,Aq$.

(1110) *Chlorinated derivatives of acetic acid.*—Acetic acid when acted on by chlorine forms two compounds, in which a portion of its hydrogen is displaced by chlorine, viz.:—

Chloracetic acid . . . . . . $HO,C_4\left.\begin{matrix}H_2\\Cl\end{matrix}\right\}O_3$,

Trichloracetic acid . . . . . $HO,C_4Cl_3O_3$.

Chloracetic Acid ($HO,C_4H_2ClO_3$: *Sp. gr. of liquid at* 163°, 1·3947) is a colourless liquid which has the odour of acetic acid. In order to obtain it, gaseous chlorine is made to act upon boiling hydrated acetic acid, whilst the mixture is exposed to the sun's rays. The gas is transmitted until it ceases to be absorbed: the excess of chlorine is then removed by means of a current of carbonic acid gas, whilst the liquid is still maintained at the boiling point. The product is submitted to fractionated distillation, and the portion which distils at 367° is the pure acid: as it cools it solidifies to a mass of deliquescent, rhomboidal, or acicular crystals fusible at about 115°. This acid forms definite salts, in the solutions of which, when dilute, a solution of nitrate of silver occasions no precipitate.

Trichloracetic Acid ($HO,C_4Cl_3O_3$); *Sp. gr. of crystals* 1·617: *of vapour* 5·3; *Boiling pt.* 392°.—This acid is usually prepared by exposing glacial acetic acid in large bottles, filled with gaseous chlorine, to the action of the sun: about one drachm of acetic acid should be used for each gallon of chlorine. A complicated reaction ensues, in which, in addition to the trichloracetic acid, oxychloride of carbon, and carbonic and oxalic acids are formed, mixed with an ethereal compound which contains chlorine. The trichloracetic acid is deposited upon the sides of the vessel in white flocculi, which are very deliquescent. It is monobasic, and forms soluble salts, many of which may be obtained in crystals; the trichloracetates, when heated, are decomposed into oxychloride of carbon and carbonic oxide, leaving a residue of a metallic chloride. For example:—

$$\overbrace{KO,C_4Cl_3O_3}^{\text{Trichloracet. potash.}} = KCl + \overbrace{C_2O_2Cl_2}^{\text{Oxychlor. carbon.}} + \overbrace{C_2O}^{\text{Carb. oxide.}}.$$

Trichloracetic acid is also produced by the oxidation of chloral by fuming nitric acid; $2\ C_4HCl_3O_2 + O_4$, becoming $2\ (HO,C_4Cl_3O_3)$, and this is one of the best modes of preparing it, since the excess of nitric acid is easily removed by distillation. After the nitric acid has been expelled, the residue is dissolved in water, and crystallized by spontaneous evaporation over sulphuric acid, *in vacuo*. Trichloracetic acid is formed also by the simultaneous action of chlorine and water on protochloride of carbon; $C_4Cl_4 + 2\ H_2O_2 + Cl_2 = 3\ HCl + (HO,C_4Cl_3O_3)$; it may likewise be procured by the decomposition of perchlorinated vinic ethers by water (1020).

The monohydrate of this acid crystallizes in colourless rhombohedra, which are fusible at 115°, and are very deliquescent; the acid has a slight odour, and an acrid sour taste. It bleaches the tongue, and if applied to the skin raises blisters. It may be distilled without decomposition, yielding a suffocating vapour.

Trichloracetic acid, when treated with an amalgam of potassium, yields chloride of potassium, and acetate of potash is reproduced:—

$$\overbrace{HO,C_4Cl_3O_3}^{\text{Trichloracet. potash.}} + 3\ K_2 + 2\ H_2O_2 = \overbrace{KO,C_4H_3O_3}^{\text{Acet. potash.}} + 3\ KCl + 2\ (KO,HO).$$

Bromacetic Acid ($HO,\ C_4H_2BrO_3$; *Boiling pt.* 406°·4) may be obtained by heating in a sealed tube for some hours to 360° a mixture of 4 volumes of crystallizable acetic acid and 1 volume of bromine, and distilling the product; hydrobromic acid escapes in abundance, and on raising the temperature the unaltered acetic acid passes over. When the boiling point reaches 406°, pure bromacetic acid is obtained, and crystallizes in rhombohedra, which are very deliquescent, and contaminated with dibromacetic acid. (Perkin and Duppa, *Q. J. Chem. Soc.*, xi. 22.)

(1111) *Sulphacetic* or *Acetosulphuric Acid* ($2\ HO,C_4H_2S_2O_8 = C_4H_4O_4,S_2O_6$).—Acetic acid combines with sulphuric anhydride and forms a dibasic acid, which may be obtained crystallized in deliquescent needles: it forms crystallizable salts. The solution of this acid is not decomposed by ebullition: it gives no precipitate with salts of lead or of lime, but with baryta it forms a crystalline compound of sparing solubility. The aceto-sulphate of silver crystallizes readily in long flattened prisms.

(1112) *Thiacetic Acid* ($C_4H_4S_2O_2 = HS,\ C_4H_3O_2S$).—When monohydrated acetic acid is acted upon by the tersulphide of phosphorus (PS_3), or the pentasulphide (PS_5), a colourless liquid is obtained which has a mingled odour of acetic acid and sulphuretted hydrogen: *it boils at about* 200°, and is soluble in water in all proportions. It has an acid reaction and a sour taste: when heated upon granulated zinc, the metal is dissolved with evolution of hydrogen; when added to a strong solution of a soluble salt of lead, a sparingly soluble monobasic lead salt is precipitated, which readily undergoes decomposition, even when dry; whilst sulphide of lead is separated. *Thiacetic anhydride* ($C_4H_3O_2S,C_4H_3O_2S$) is obtained by distilling pentasulphide of phosphorus with acetic anhydride. It is a colourless oily liquid, which boils at 250°, and emits an odour similar to that of its hydrate. It is heavier than water, which gradually decomposes it into a mixture of hydrated acetic and thiacetic acids. (Kekulé, *Proceed. Roy. Soc.*, vol. vii. p. 37.)

$$\overbrace{(C_4H_3O_2S,C_4H_3O_2S)}^{\text{Thiacetic anhydride.}} + H_2O_2 = \overbrace{(HO,C_4H_3O_3)}^{\text{Acetic acid.}} + \overbrace{(HS,C_4H_3O_2S)}^{\text{Thiacetic acid.}}.$$

This compound is only one of a series which may be obtained by similar means from other acids homologous with the acetic: in this way *thioformic* acid (HS,C_2HO_2S) has been obtained. Thiacetic acid may be regarded as ordinary hydrated acetic acid in which the basic water has been displaced by sulphuretted hydrogen; at the same time one of the equivalents of oxygen in the acid itself has been displaced by an equivalent of sulphur:—

If acetic acid be represented as . . . $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$

Thiacetic acid would be . . . . . $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}S_2$.

This confirms the view of Gerhardt that the radicle of the volatile fatty acids is to be regarded rather as ($C_{2n}H_{2n-1}O_2$) than as ($C_{2n}H_{2n-1}$): the radicle of acetic acid being ($C_4H_3O_2$) instead of (C_4H_3), for hitherto one atom only out of the three of oxygen present has been displaced by chlorine, or by sulphur; acetic oxychloride, for example, being $C_4H_3O_2Cl$ (1094).

(1113) 3. *Propionic,* Propylic, Metacetic,* or *Metacetonic Acid* ($HO,C_6H_5O_3=9+65$).—This acid is formed in a variety of ways; for example, it is one of the products of the oxidation of oleic acid; and it is also obtained by the action of potash upon hydrocyanic ether. In the latter case, ammonia is liberated and propionate of potash is formed:—

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* *From* πρῶτος first, πίων fat, because the first or simplest in the series of *the true fatty* acids.

$$\overbrace{C_4H_5,C_2N}^{\text{Cyanide of ethyl.}} + H_2O_2 + KO,HO = \overbrace{KO,C_6H_5O_3}^{\text{Propionate of potash.}} + H_3N\,;$$

a concentrated alcoholic solution of potash is to be heated in a tubulated retort, and cyanide of ethyl added drop by drop; the distillate is to be returned into the retort until the odour of cyanide of ethyl has disappeared: the residue of propionate of potash, when distilled with syrupy phosphoric acid, yields pure propionic acid.

Propionic acid may also be obtained as Wanklyn has shown by acting upon sodium-ethyl by means of carbonic acid, when propionate of soda is the result (1026). Another interesting reaction which furnishes propionic acid is that which establishes the connexion between lactic and propionic acids;* when lactic oxychloride is decomposed by water it furnishes chloropropionic acid, and if treated with finely granulated zinc the chloropropionic acid is reduced to propionic acid (Ulrich):—

$$\overbrace{C_6H_4O_2,Cl_2}^{\text{Lactic oxychloride.}} + H_2O_2 = \overbrace{C_6H_5ClO_4}^{\text{Chloropropionic acid.}} + HCl\,; \text{ and}$$

$$\overbrace{C_6H_5ClO_4}^{\text{Chloropropionic acid.}} + H_2 = \overbrace{C_6H_6O_4}^{\text{Propionic acid.}} + HCl.$$

If the liquid be decanted from the zinc as soon as the odour of the chlorinated compound has disappeared, and be distilled, propionic acid, with traces of hydrochloric acid, comes over freely. A more convenient means of obtaining propionic acid consists in distilling 3·5 parts of lactic acid with 4 of biniodide of phosphorus. Iodine and water are liberated, and propionic acid is formed, whilst phosphorous acid remains in the retort.

Strecker has likewise observed the formation of this acid by the fermentation of a mixture of lactate of lime and mannite, which had been set aside with the view of procuring butyric acid. Crude tartrate of lime in warm weather frequently undergoes a species of fermentation, and furnishes propionic acid. The acid is also produced during the fermentation of glycerin (1067). Metacetone [$(C_6H_5O)_2$; 934] when oxidized with a mixture of bichromate of potash and sulphuric acid, also yields the acid, which derived its name of metacetonic acid from this circumstance. Propionic acid, when prepared from these sources, is liable to be contaminated with acetic and other acids homologous with it. The acetic acid may be removed by saturating the distilled liquid with carbonate of soda, and evaporating to the crystallizing point; the acetate of soda crystallizes out, whilst the propionate remains in the mother liquor, from which propionic acid may be procured by distillation with sulphuric acid.

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* Lactic acid, $C_6H_6O_6$, contains 2 atoms more of oxygen than the propionic, $C_6H_6O_4$. *Kolbe calls it oxypropionic* acid.

Hydrated propionic acid ($HO,C_6H_5O_3$) crystallizes in plates which melt on the application of a gentle heat; at a temperature of 284° it boils and may be distilled: it has a powerfully acid taste, and a pungent odour which is intermediate between that of butyric and of acrylic acids. Propionic acid is largely soluble in water, but, when this liquid is saturated with it, the excess of the acid floats like an oil upon the surface.

Most of the propionates are soluble and crystallizable. The propionates of *potash* and *soda* are deliquescent. *Propionate of lime* is efflorescent, but very soluble. *Propionate of baryta* is anhydrous and very soluble; it crystallizes in prisms, which when thrown into water are dissolved with a gyratory motion. *Propionate of copper* ($CuO,C_6H_5O_3+Aq$) crystallizes in oblique prisms, which are readily soluble in alcohol, but very slightly so in water. *Propionate of silver* is anhydrous, and less soluble than the acetate; it crystallizes in tufts of short needles, and blackens by exposure to light; but the acetate and the propionate of silver cannot be separated by crystallization, for they unite and form a double salt, which is deposited from a hot solution in brilliant dendritic needles.

A *nitro-propionic acid*, $HO,C_6\left.\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_3$, may be obtained as a heavy yellow, sparingly soluble oil, by treating butyrone, $C_{14}H_{14}O_2$, with nitric acid. Its salts detonate feebly when heated.

(1114) 4. BUTYRIC ACID ($HO,C_8H_7O_3=9+79$); *Sp. gr. of liquid at* 32°, 0·9886; *of vapour* 3·07.—This acid is a liquid which, at 59°, has the sp. gr 0·963; it remains fluid at —4° F., and volatilizes at ordinary temperatures with a strong smell of rancid butter; it boils at 314°·6 F. (Kopp), and may be distilled unchanged. Butyric acid has a sharp acrid taste, and a corrosive action upon the skin; it is readily soluble in water, alcohol, and ether: the addition of a solution of hydrochloric acid or of chloride of calcium to its aqueous solution causes the butyric acid to separate and rise to the surface. It was originally procured from butter by saponifying that portion of it which remained liquid at 60°, adding hydrochloric or tartaric acid and distilling; the distillate, consisting of a mixture of caproic, caprylic and capric with butyric acid, is treated with baryta, and the baryta salts separated by crystallization in the mode directed under the head caproic acid (1126). The acid is however more easily obtained in a state of purity by distilling 3 parts of the butyrate of lime produced by the fermentation of sugar, with 12 parts of water and 1 of concentrated hydrochloric acid: about 3 parts of liquid should be distilled over. If the distillate be digested upon an excess of chloride of calcium, the solution which is formed separates into two layers, the upper one of which contains the butyric acid: it must be decanted into a retort and distilled: the first portions which pass over are aqueous, but when the temperature rises to 327° (Gélis and Pelouze), the acid passes over in the concentrated form ($HO,C_8H_7O_3$).

Butyric anhydride ($C_8H_7O_3,C_8H_7O_3$); *Sp. gr. of liquid at* 54°, 0·978; *of vapour* 5·38; *Boiling pt.* 374°.—This body may be obtained by distilling a mixture of five parts of chloride of benzoyl, and eight of dry butyrate of soda: it forms a colourless, very mobile liquid, with an odour which resembles that of the pine-apple. When exposed to the air it absorbs moisture and acquires the repulsive odour of the hydrated acid.

Butyrates.—Butyric acid is monobasic. Its salts when dry are without odour; but when moist they have a smell of rancid butter. Most of them are very freely soluble; when reduced to powder, and thrown upon water, they are dissolved with a rapid gyratory motion. *Butyrate of baryta* crystallizes, by spontaneous evaporation, in long prisms, with 4 Aq; when formed by the cooling of a hot solution it retains only 2 Aq.* *Butyrate of zinc* crystallizes in anhydrous, very soluble, pearly tables, which when heated to 212° fuse and then lose part of their acid, after which a portion of the salt undergoes sublimation in the anhydrous form. *Butyrate of copper* ($CuO,C_8H_7O_3+2\,Aq$) is bluish green and sparingly soluble. With *lead*, butyric acid forms two anhydrous salts, one of which is normal, while the other contains three equivalents of base. The butyrates of *suboxide of mercury* and of *silver* are sparingly soluble; they crystallize in brilliant plates. But the most characteristic salt of butyric acid is the *butyrate of lime*, which forms fusible colourless needles, which are rendered anhydrous by a temperature of 284°: this salt is much less soluble in boiling water than it is at ordinary temperatures, and when its aqueous solution is boiled, a large proportion of the salt is precipitated, and is redissolved as the liquid cools. Butyric acid is remarkable for the facility with which it effects the etherification of alcohol. If a mixture of 2 parts of concentrated butyric acid, 2 of alcohol, and 1 part of oil of vitriol be agitated together, butyric ether is formed and rises to the surface on standing. It may be purified by washing and rectification from chloride of calcium. This ether in a dilute form has the aroma of the pine-apple; it appears to be present in old rum, and is used for heightening the flavour of this spirit. The melon and strawberry are supposed to owe a portion of their flavour to the presence of this compound. Many of the butyrates when submitted to dry distillation yield *butyrone* ($C_{14}H_{14}O_2$), a colourless liquid insoluble in water, of sp. gr. 0·83; boiling at 291°; and emitting a vapour of sp. gr. 3·99.

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* On one occasion I obtained it crystallized in anhydrous square tables, presenting the appearance of the square base of the octohedron. They were, however, in reality macled crystals formed by the junction of two nearly rectangular rhombic tables. In other cases the salt forms fibrous crystals which are also anhydrous.

Chlorine acts readily upon butyric acid in the sunlight, and forms two substitution acids which are analogous to butyric acid, and which yield corresponding monobasic salts; these acids are the dichlorobutyric ($HO,C_8H_5Cl_2O_3$), and tetrachlorobutyric acids ($HO,C_8H_3Cl_4O_3$). Nitric acid converts the butyric into *nitrobutyric* acid ($HO,C_8H_6NO_4,O_3$).

Butyric acid exists ready formed in certain fruits, and it is one of the products of oxidation of azotised matters, such as fibrin or casein, when treated with oxide of manganese and sulphuric acid; it is also obtained amongst the results of the action of nitric upon oleic acid. All substances which furnish lactic acid may be made to yield the butyric; and it is frequently developed during the fermentation or decay of many mucilaginous and amylaceous roots, such as the potato and the mallow. Butyric acid may be obtained at pleasure in large quantities, by the following method of fermenting sugar discovered by Pelouze and Gélis (*Ann. de Chimie*, III. x. 434). A solution of 4lb. of sugar in a quantity of water sufficient to form a liquid of sp. gr. 1·070, is mixed with a quantity of poor cheese which in its dry state would contain casein to the extent of one-eighth of the weight of the sugar used, and 2lb. of chalk; the whole is then exposed for some weeks to a temperature ranging between 80° and 90° F. The liquid speedily becomes ropy, lactic acid is formed abundantly, and combines with the lime, the mixture becoming semisolid owing to the formation of crystals of lactate of lime; this salt in turn undergoes decomposition, and when this second reaction commences, a mixture of carbonic acid and hydrogen escapes from the fermenting mass, whilst butyrate of lime is formed in abundance. This reaction is explained by the following equation:—

$$2\,\overbrace{(HO,C_6H_5O_6)}^{\text{Lactic acid.}} = \overbrace{HO,C_8H_7O_3}^{\text{Butyric acid.}} + 2\,C_2O_4 + 2\,H_2.$$

Pasteur believes this conversion of lactic into butyric acid to ffected by the agency of a special ferment consisting of orial animalculæ in the form of small cylindrical bodies, h sometimes are connected together in chains of four or .

1115) 5. VALERIC, or VALERIANIC ACID ($HO,C_{10}H_9O_3=$ 3): *Sp. gr. of liquid* 0·937; *of vapour* 3·66; *Boiling pt.* 347°. is compound appears to be identical with the *phocenic* acid ned by Chevreul from some of the fish oils. It occurs also ciated with a peculiar essential oil) in the root of the valerian; likewise present in the berries of the guelder-rose (*Viburnum s*). If valerian root be distilled with water acidulated with sulphuric acid, valeric acid passes over into the receiver: antity may be increased by digesting the root with a mixture ute sulphuric acid and bichromate of potash, since the valerian contains a compound (valerol, $C_{12}H_{10}O_2$), which by oxidation mes converted into valeric acid. Valeric acid is also a fre- t product of the oxidation of oleic acid and of other fatty acids; likewise often present in decaying cheese, but it is most ly obtained by the action of oxidizing agents on amylic alcohol. e vapours of fousel oil be sent through a tube, filled with a ure of lime and hydrate of soda and heated to 400°, valerate da is produced, and hydrogen, mixed with carburetted gen, is evolved. When cold, the mass must be plunged at into water to prevent it from taking fire by access of air; the solution must be distilled with dilute sulphuric acid: ic acid then passes over into the receiver. A still easier hod of preparing it consists in distilling fousel oil with a mix- of dilute sulphuric acid and bichromate of potash; valeric mixed with valerate of amyl ($C_{10}H_{11}O,C_{10}H_9O_3$) passes over, the latter may be decomposed by potash into valerate of h and fousel oil. The valerate of potash when distilled with huric acid furnishes pure valeric acid.

Valeric acid is a limpid colourless oil, which remains liquid at It has a powerful odour allied to that of valerian root, and a g taste. It may be distilled without change. It is spar- luble in water, but is soluble in alcohol and in ether in all ions: it is also freely soluble in strong acetic acid. acid resembles the acetic in its property of forming a ydrate ($HO,C_{10}H_9O_3+2\,Aq$), *which* is obtained when the acid is liberated by a stronger acid from an aqueous solution of salts.

Valeric anhydride ($C_{10}H_9O_3,C_{10}H_9O_3$; *Sp. gr. of liquid* *of vapour* 6·23° ; *Boiling pt.* 419°) is a colourless, mobile li with an agreeable odour of apples ; the alkalies in the presen water rapidly convert it into a hydrate. This compound is obtained by allowing 1 part of oxychloride of phosphorus to drop by drop upon 6 parts of dry valerate of potash ; wa the product with a weak solution of carbonate of soda, and dissolving out the anhydride with ether: the ethereal soluti agitated with fused chloride of calcium in order to re water ; and on expelling the ether by heat, the anhydride is in a state of purity.

The valerates when dry are destitute of odour, they ha sweetish taste, and are easily recognised by the peculiar sme valeric acid which they emit when heated with dilute sulph acid. These salts, with the exception of the valerates of and of suboxide of mercury, are soluble in water, and ma them are also soluble in alcohol. Those of the alkalies are quescent, and crystallize with difficulty ; they fuse readily on application of a moderate heat. Valerate of baryta (BaO,C + 2 Aq) crystallizes in prisms, which are brittle. Valerate zinc crystallizes in anhydrous plates ; this salt, as well as others of the valerates, has been used medicinally.

Chlorine acts upon valeric acid by displacing a portion of hydrogen ; by this means two new substitution compounds ma formed. Both of these bodies retain the monobasic characte valeric acid. They were termed by Dumas, *chlorovalerisic* ($C_{10}H_6Cl_3O_3$) and *chlorovalerosic* ($HO,C_{10}H_5Cl_4O_3$) acids ; bo them form stable, well-defined salts.

When valeric acid is boiled for several days with concentr nitric acid it becomes decomposed, and a great part is conve into *nitrovaleric acid* [$HO,C_{10}H_8(NO_4)O_3$], which is vo without decomposition ; it crystallizes in beautiful rhombo tables, and forms definite salts.

(1116) 6. *Caproic Acid* ($HO,C_{12}H_{11}O_3$); *Sp. gr. of vapour* —This acid is liquid at ordinary temperatures : it has a cha teristic odour of acid sweat, and has a pungent and sweetish the concentrated acid bleaches those parts of the tongue whi touches. It boils at about 392°, and may be distilled uncha Water dissolves it to a small extent. Caproic acid is obtain small quantity by the saponification of butter, or of cocoa-n and it is amongst the volatile products of the oxidation of ol

l. It may be obtained from butter by pressing out the hich remains liquid at 60°, then saponifying this oil, and the soap with sulphuric acid; capric, caprylic, caproic, ric acids are thus obtained in the liquid which passes e distillate is to be neutralized with baryta, which forms caproate, whilst the caprylate and caprate are nearly in- The caproate and butyrate are separated by crystalliza- aproate assuming the form of delicate, brilliant, anhy- dles, if the solution be evaporated above 86°, whilst if ontaneous evaporation, it forms hexagonal plates which in the atmosphere. Anhydrous caproate of baryta, if ith perchloride of phosphorus, yields *caproic anhydride* $C_{12}H_{11}O_3$), in the form of a colourless neutral oil, which water, by which it is rapidly converted into the hydrated proate of silver is sparingly soluble, but most of the s of the acid are readily dissolved by water.

) 7. *Œnanthylic Acid* ($HO,C_{14}H_{13}O_3$).—This acid is s one of the products of the oxidation of oleic acid by nitric acid. It is also produced during the destructive n of castor oil; but it is most readily obtained by heat- art of castor oil in a retort with two parts of concen- ric acid diluted with twice its volume of water. A brisk occurs; the mixture must be maintained at a boiling re for a few hours, and the products which distil over mixed with water, when an oily stratum of œnanthylic rise to the surface; it must be again distilled with water, be obtained as a monohydrate by distilling the liquid ial phosphoric acid.

thylic anhydride ($C_{14}H_{13}O_3,C_{14}H_{13}O_3$) may be obtained liquid of sp. gr. 0·92, by distilling œnanthylate of potash hloride of phosphorus. *Hydrated* œnanthylic acid may d to a cold of 0° without becoming solid; it boils and istilled at 298°, but it undergoes partial decomposition e operation. One of its most characteristic salts is the ate of copper, which crystallizes in beautiful green these are soluble in alcohol, but nearly insoluble in

) 8. *Caprylic Acid* ($HO,C_{16}H_{15}O_3=9+135$: *Sp. gr. of* 31) was one of the volatile acids obtained by Chevreul e saponification of butter; it is found likewise in cocoa- s well as amongst the products of the oxidation of oleic itric acid.

ylic anhydride ($C_{16}H_{15}O_3,C_{16}H_{15}O_3$) is a limpid oil of a disagreeable odour, which burns with a luminous flame: it becomes solid in the cold produced by a mixture of ice and salt. *Hydrated* caprylic acid becomes solid at about 54°, it melts at 58° or 59°, and boils and may be distilled at 457°: it is but sparingly soluble in water even at a temperature of 212°. It is best prepared by decomposing the caprylate of baryta with sulphuric acid: caprylate of baryta is insoluble in alcohol and in ether, but is dissolved by twice its weight of boiling water; it crystallizes from its aqueous solution in anhydrous colourless plates, which are deposited in rounded nodular masses. Caprylic acid is usually accompanied by capric acid, but since the caprylate of baryta is more soluble than the caprate of this base, the acids may be separated by converting them into baryta salts and then crystallizing them.

(1119) 9. *Pelargonic Acid* ($HO,C_{18}H_{17}O_3$).—This acid was originally extracted from the leaves of the geranium, by distilling them with water, purifying the oil which floats on the surface by neutralizing it with hydrate of baryta, and heating the mixture to drive off a volatile oily body which comes over with the acid. The pelargonate of baryta is afterwards decomposed by an acid. Pelargonic acid may also be prepared by heating oil of rue with an equal measure of nitric acid which has been diluted with its own bulk of water; and it is also produced by the oxidation of oleic acid by the same reagent. *Pelargonic anhydride* ($C_{18}H_{17}O_3$, $C_{18}H_{17}O_3$) is a colourless oil which solidifies at 32°, and has a disagreeable odour of rancid butter: it is obtained by acting upon pelargonate of baryta with oxychloride of phosphorus. *Hydrated pelargonic* acid is a colourless oil which is nearly insoluble in water, but soluble in alcohol and ether: it has a faint unpleasant smell; at 500° it boils, and may be distilled unchanged: according to Delffs it is identical with the œnanthic acid of Liebig and Pelouze, but this is doubtful.

(1120) 10. *Capric,* or *Rutic acid* ($HO,C_{20}H_{19}O_3$) is a volatile fatty acid which possesses many interesting relations to other bodies. It was discovered by Chevreul amongst the products of the saponification of butter; but it is also furnished by the oxidation of oleic acid by nitric acid, and Gerhardt has procured it readily by acting upon oil of rue with fuming nitric acid; one of the constituents of oil of rue* ($C_{20}H_{20}O_2$), having, according to Gerhardt, the composition of the aldehyd of capric acid: during the oxidation of oil of rue by nitric acid, a portion of pelargonic acid is usually formed at the same time. Capric acid is also contained in small quantity in the fatty acids of the cocoa-nut oil. Capric acid crystallizes in colourless needles, which are fusible at 86°; it has a slight odour of the goat. This acid is sparingly soluble in boiling water, but it separates completely, in glistening plates, as the liquid cools; its taste is sour and burning. It is soluble in alcohol in all proportions: when distilled it is liable to undergo partial decomposition. Capric acid is generally purified by causing it to combine with baryta; the salt thus obtained crystallizes in brilliant plates: it is soluble to a considerable extent in boiling water, but requires 200 parts of cold water for solution.

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* According to Greville Williams, oil of rue consists chiefly of *euodic aldehyd* ($C_{22}H_{22}O_2$), mixed with a small quantity of lauric aldehyd ($C_{24}H_{24}O_2$), besides a hydrocarbon isomeric with oil of turpentine and with borneol.

12. *Lauric acid* [$HO,C_{24}H_{23}O_3$; *fusing point* 110° (Heintz)] was first extracted from the soft green fat of the bay berries (*Laurus nobilis*), but it has since been found in cocoa-nut oil (Georgey), as well as in the pichurim nut, and in cacao butter.

14. *Myristic acid* ($HO,C_{28}H_{27}O_3$) is comparatively unimportant; it is furnished by nutmeg butter, and fuses at 129° (Heintz).

(1121) 16. PALMITIC ACID ($HO,C_{32}H_{31}O_3=9+247$).—This acid is obtained most readily from palm oil, the solid portion of which consists chiefly of the glycerin compound of palmitic acid, and which, when long kept, often contains the free acid in large quantity, amounting in some instances to one-third of its weight. Under these circumstances the oil contains a considerable quantity of uncombined glycerin. Palmitic acid may also be procured by the saponification of spermaceti: according to Heintz, it is likewise present in human fat, in the solid constituent of olive oil, and generally in substances which have been described as yielding margarin. It is likewise one of the products of the decomposition of oleic acid when this body is fused with twice its weight of hydrate of potash:—

$$\overbrace{HO,C_{36}H_{33}O_3}^{\text{Oleic acid.}}+2\,(KO,HO)=\overbrace{KO,C_{32}H_{31}O_3}^{\text{Palmit. potash.}}+\overbrace{KO,C_4H_3O_3}^{\text{Acet. potash.}}+H_2.$$

Palmitic acid, after repeated crystallization from alcohol, appears as a tasteless white fat, which may be obtained in tufts of delicate needles, fusible at 143°·6. It may, with care, be distilled without undergoing decomposition.

The neutral palmitates of the alkalies are readily soluble in hot water, and form solutions which gelatinize on cooling. They are sparingly soluble in cold alcohol, but freely so in boiling alcohol: this solution deposits the salts in crystals on cooling. The aqueous solutions of the normal palmitates, when largely diluted with water, are decomposed in a manner similar to those of the stearates, into an insoluble acid salt, whilst a portion of the base remains in solution.

(1122) 17. MARGARIC ACID ($HO,C_{34}H_{33}O_3$).—In order to prepare this substance, Marseilles, or olive-oil soap, is to be dissolved in boiling water, and mixed with a solution of chloride of calcium; a precipitate of mingled oleate and margarate of lime is thus obtained, which after being dried is pulverized and digested in cold ether, so long as anything is dissolved: the oleate of lime is thus brought into solution, whilst the margarate is left behind. The margarate is then decomposed by boiling it with hydrochloric acid, and the oily acid which separates is thoroughly washed, and recrystallized from alcohol: as thus obtained it melts at 140° F. Heintz, however, states that the acid so obtained may be separated into stearic and palmitic acid, by repeatedly crystallizing it from alcohol; the melting point may thus be raised till it reaches 159°, the fusing point of stearic acid. A better plan consists in adding to a boiling solution of the acid in alcohol a boiling solution of acetate of lead, or of acetate of baryta, containing a quantity of the baryta, or lead salt, amounting to two-sevenths of the weight of the fatty acid. As the liquid cools, a precipitate is obtained, which is to be collected upon a filter. This portion contains the whole of the stearic acid, whilst most of the palmitic acid remains in solution; the filtered liquid is now to be precipitated by an excess of the baryta or lead salt. This latter precipitate contains the palmitic acid; it may be decomposed by hydrochloric acid, and recrystallized from alcohol till its melting point remains fixed at 143°·6. If necessary, it may be again submitted to a partial precipitation with acetate of lead, or of baryta.

Although the melting point of stearic acid is 159°, and that of palmitic acid is 143°·6, Heintz finds that a mixture of the two acids melts at a lower temperature than either of them separately; and if 9 or 10 parts of palmitic acid be fused with 1 part of stearic acid, a mass is obtained which solidifies at 140°; which corresponds to the fusing point of the so-called margaric acid.

Becker, however, considers that he has obtained margaric acid artificially by decomposing cyanide of cetyl by means of hydrate of potash; $C_{32}H_{33},C_2N + KO,HO + H_2O_2 = KO,C_{34}H_{33}O_3 + H_3N$. The fusing point of this acid was as low as 127°.

(1123) 18. STEARIC ACID ($HO,C_{36}H_{35}O_3 = 9 + 275$).—This important fatty acid is liberated during the saponification of all the fats which contain stearin. Until recently it was regarded as a dibasic acid, and its formula was represented as ($2\,HO,C_{68}H_{66}O_5$). It may, however, with care, be distilled without decomposition, and further experiments by Heintz and others have shown that it belongs to the same series of acids as the palmitic, which it greatly resembles. The *bassic acid,* which Hardwich extracted from the oil of the *Bassia latifolia,* and found to possess the formula ($HO,C_{36}H_{35}O_3$), is pure stearic acid.

Stearic acid may be obtained by saponifying mutton suet, and decomposing the hot solution of the soap with hydrochloric, or still better, with tartaric acid. The oily acids are next to be submitted to pressure between hot plates, by which means a large portion of the oleic acid is separated: the solid residue is then to be recrystallized from alcohol, three or four times, and afterwards from ether, until the fusing point becomes constant at 159°. The ethereal solution, if allowed to cool very slowly, deposits the acid in beautiful colourless, transparent, rhombic plates. When fused it presents the appearance of a colourless oil, destitute of taste or odour; and, on solidifying, it concretes into a white crystalline mass, which is insoluble in water, but freely soluble in hot alcohol: this solution reddens litmus.

Stearates.—Stearic acid forms both normal and acid salts. The stearates of the alkalies are soluble in a small quantity of water, and in alcohol; a mixture of alcohol and ether, of sp. gr. 0·750, also dissolves them, and deposits them in crystals on cooling. When an aqueous solution of normal stearate of potash or of soda is largely diluted with water, the liquid becomes turbid, and a copious separation of silky crystalline plates of an acid stearate of the base is occasioned. Chevreul, who has carefully examined this decomposition, finds that it is not an isolated case, but that generally, when a salt is formed by the union of a base soluble in water with an acid which is insoluble, the normal salt so obtained is decomposed by water, with the precipitation of an insoluble acid salt, while a portion of the base remains in solution.

Stearate of soda is the basis of ordinary hard soap. The soluble stearates are separated from their solution in water by the addition of a large excess of soda or of potash. Chloride of sodium also causes their immediate coagulation; and some other salts have a similar effect: advantage is taken of this fact to separate soap from glycerin and other impurities in the operation of soap-making.

The other stearates are insoluble; those of baryta and lime are crystalline, and insoluble in alcohol. Stearate of magnesia is fusible, and may be dissolved by boiling alcohol. Stearate of lead is easily formed by adding a solution of acetate of lead to one of stearate of soda: it is a heavy amorphous precipitate, fusible at about 260°, sparingly soluble in alcohol and in ether, but readily soluble in oil of turpentine; stearate of lead is one of the constituents of the ordinary lead plaster.

Stearic acid, when submitted for some weeks to a current of chlorine, at a temperature of 212°, loses a portion of its hydrogen, and becomes converted into a yellowish, transparent, chlorinated compound, of a resinous aspect, in which Hardwich found that 10 atoms of hydrogen had been displaced by 10 of chlorine, forming *chlorostearic acid* ($HO,C_{36}H_{25}Cl_{10}O_3$).

When stearic acid is boiled for some days with nitric acid, it is gradually converted into succinic and suberic acids (1130, 1133). It has been stated that it may be converted into margaric acid by gently heating it for a short time with nitric acid, but Heintz has shown that this is an error.

Arachidic or *butic acid* ($HO,C_{40}H_{39}O_3$) does not appear to have been obtained from butter in a state of perfect purity; but a crystallizable fatty acid having the composition assigned to it has been extracted from the oil obtained from the seeds of the *Arachis hypogæa*, the ground-nut oil of Western Africa.

Melissic and *cerotic* acids have been already described (1055).

(*b*) *Acids of the Oleic Series*, $HO,(C_{2n}H_{2n-3})O_3$.

(1124) The acids which belong to this group have been less perfectly studied than those of the foregoing one. Oleic acid is the most important member of this series. Owing to the facility with which these acids absorb oxygen, and the difficulty of purifying them from the results of this oxidation on account of their indisposition to crystallize, the investigation of these compounds is attended with considerable difficulty. The higher terms of this series are decomposed, when they are heated with a view to effect their distillation.

The acids of this group are characterized by their tendency when heated gently with hydrate of potash, to break up into acetic acid and a second acid of the stearic series, whilst hydrogen is liberated. Oleic acid in this manner yields acetic and palmitic acids:—

$$\overbrace{HO,C_{36}H_{33}O_3}^{\text{Oleic acid.}}+2\,(KO,HO)=\overbrace{KO,C_4H_3O_3}^{\substack{\text{Acetate}\\ \text{of potash.}}}+\overbrace{KO,C_{32}H_{31}O_3}^{\substack{\text{Palmitate}\\ \text{of potash.}}}+H_2.$$

Acrylic acid when similarly treated yields acetic and formic acids:—

$$\overbrace{HO,C_6H_3O_3}^{\text{Acrylic acid.}} + 2\,(KO,HO) = \overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}} + \overbrace{KO,C_2HO_3}^{\text{Formiate of potash.}} + H_2.$$

The acids of this group possess the remarkable property of being converted by peroxide of nitrogen into metameric acids, which require a much higher temperature for their fusion than the oily acids from which they were obtained. These solid acids may be distilled unchanged. When these less fusible metameric acids are heated with hydrate of potash, they also undergo decomposition into acetic acid, and another acid of the stearic series; hydrogen being evolved, exactly as in the case of their more fusible metamerides.

The following table contains the names of the acids of both isomeric series which are at present known. The formulæ of some of the higher terms will probably be modified hereafter, and the number of equivalents of carbon will possibly in all these cases be found to be divisible by four:—

Acids of the Oleic Series ($HO,C_{2n}H_{2n-3}O_3$), or ($C_{2n}H_{2n-2}O_4$).

Liquid Acids.				Metameric solid Acids.			
		Fusing point.	Origin.			Fusing point.	Origin.
Acrylic .	$C_6H_4O_4$		Distillation of glycerin.				
Moringic .	$C_{30}H_{28}O_4$		Oil of Ben.				
Physetoleic	$C_{32}H_{30}O_4$	32°	Sperm whale.	Angelic	$C_{10}H_8O_4$	113°	Angelica root.
Oleic . .	$C_{36}H_{34}O_4$	57°	Non-drying oils.	Elaidic	$C_{36}H_{34}O_4$	113°	Action of (NO_4) on oleic acid.
Doeglic .	$C_{38}H_{36}O_4$	62°	The Dögling whale.				
Erucic .	$C_{44}H_{42}O_4$	93°	Mustard seed and rapeseed.				

(1125) It will not be necessary to dwell long upon any acid of this group except the oleic.

Acrylic acid ($HO,C_6H_3O_3$) is obtained by the oxidation of acrolein (1071). This is best effected by digesting acrolein on oxide of silver in excess; the pungent smell of acrolein disappears, and acrylate of silver is obtained in solution, whilst metallic silver is deposited, and water is eliminated:—

$$\overbrace{2\,(C_6H_3O_2,H)}^{\text{Acrolein.}} + 3\,Ag_2O_2 = 2\,(\overbrace{AgO,C_6H_3O_3}^{\text{Acrylate of silver.}}) + 2\,Ag_2 + H_2O_2.$$

If the acrylate of silver be placed in a bulb tube, kept cool by immersion in ice, it may be decomposed by transmitting over it a very slow current of sulphuretted hydrogen: sulphide of silver is formed, whilst hydrated acrylic acid is liberated; the latter may be distilled by a gentle heat. Acrylic acid has an agreeable acid odour and a burning taste. It requires a temperature below 32° to freeze it. Its boiling point is above 212°, and it may be distilled unchanged. All its salts are soluble: the salt of silver is one of the most characteristic compounds of this acid; it crystallizes in anhydrous silken needles, which much resemble the acetate of silver in appearance; it is sparingly soluble in cold water: boiling water decomposes it, and partially reduces the silver. Acrylate of silver may readily be formed from the crude products of the distillation of oils; the distillate is rectified, and those portions which come over between 100° and 140° are collected separately; they are rectified anew from chloride of calcium, and are then digested on an excess of oxide of silver, returning the portions which distil, until the pungent odour of acrolein has disappeared: water is next added, and the liquid is distilled to carry off the volatile oils; after which the boiling liquid is filtered, and set aside in a dark place to crystallize. *Acrylate of soda* crystallizes with 5 Aq in efflorescent prisms which are very soluble. *Acrylate of baryta* does not crystallize.

Angelic acid ($HO,C_{10}H_7O_3$) is met with in the root of various kinds of *Angelica;* it is also produced by the action of hydrate of potash, aided by a gentle heat, upon the oxidized principle in the essence of camomile:—

$$\overbrace{C_{10}H_8O_2}^{\text{Ess. camomile.}} + KO,HO = \overbrace{KO,C_{10}H_7O_3}^{\text{Angelate of potash.}} + H_2.$$

Angelic acid forms large, striated, colourless prisms, which fuse at 113°; it boils at 374°, and may be distilled without undergoing decomposition. It is sparingly soluble in cold water, but freely so in boiling water. When heated with hydrate of potash, it is decomposed with escape of hydrogen into acetate and propionate of potash, in accordance with the general mode of decomposition of the oleic series. From its high fusing point, and from the possibility of distilling it without decomposition, it is, however, obvious that it does not belong to the oleic series, but probably to the elaidic group.

Moringic acid ($HO,C_{30}H_{27}O_3$) is the liquid acid extracted from the oil of ben (*Moringa aptera*); it becomes solid at 32°. Oil of ben, from its indisposition to become rancid, has been used as the basis of Macassar oil.

Physetoleic acid ($HO,C_{32}H_{29}O_3$) was obtained from the oil of the ordinary sperm whale (*Physeter macrocephalus*). According to

Gössman the oil of the ground nut contains an acid of the same composition as the physetoleic, but fusing about 95°.

Doeglic acid was extracted by Scharling from the oil of the *Balæna rostrata* (in Danish, *Dögling*), a species of sperm whale. The composition of this oil is remarkable, since it does not furnish glycerin when saponified, but a compound, $HO,C_{24}H_{25}O$, which corresponds in composition to lauric alcohol. The oil when distilled gives no acrolein, showing the absence of glycerin.

Erucic acid ($HO,C_{44}H_{41}O_3$) is extracted from the oil of the white and black mustard seed, and from colza oil. It is liquid at temperatures above 93°.

(1126) OLEIC ACID ($HO,C_{36}H_{33}O_3=9+273$).—The isolation of this acid in a state of purity is a matter of some difficulty, owing to its tendency to combine with oxygen. Oleic acid is obtained in a crude form as a secondary product in the manufacture of stearin candles. In order to obtain the pure acid, Varrentrapp recommends that almond oil be saponified with potash or with soda, and that the soap be decomposed with hydrochloric acid. The mixed fatty acids are then to be digested with half their weight of finely powdered oxide of lead. On digesting the mixed salts of lead with twice their volume of ether for 24 hours, the oleate of lead is dissolved and separated from the other salts. The ethereal solution is then to be mixed with dilute hydrochloric acid, which decomposes the oleate; the oily acid is dissolved by the ether and rises to the surface. The ether is to be expelled by heat, and the acid is again to be converted into soap by the addition of an alkali; after which it is separated from its aqueous solution by the addition of chloride of sodium, pressed, redissolved in water which has been boiled for some time to expel the air, and finally decomposed by tartaric acid in vessels filled with carbonic acid gas. The acid thus obtained always has a brown colour, owing to the action of the atmospheric oxygen upon it. Gottlieb purified it by adding to the acid thus obtained a large excess of ammonia, and then precipitating it by means of chloride of barium: the oleate of baryta thus procured is dried and boiled with alcohol. During this operation the salt melts and forms a viscous liquid, but a portion of it is dissolved and is deposited in crystalline plates as the liquid cools; these are again crystallized from alcohol, and on decomposing them with tartaric acid pure oleic acid is obtained. The alcohol in the preceding operation retains the impurities which render the ordinary oleate of baryta so fusible: pure oleate of baryta is not fusible at 212°.

Pure oleic acid, at temperatures above 57°, forms a colourless, limpid oil, without taste or smell; it does not redden litmus even when dissolved in alcohol: at 40° it concretes into a hard crystalline mass, composed of fine needles. When solid it undergoes no change in the air, but when liquid it absorbs oxygen rapidly, acquiring a brown colour, a rancid odour, and an acid reaction upon litmus, its point of solidification gradually becoming lowered until it falls below 0° F. Oleic acid cannot be distilled without undergoing decomposition: a large quantity of liquid and of gaseous hydrocarbons are given off in the distillation, besides several acids of the series $C_{2n}H_{2n}O_4$, but the most characteristic product is sebacic acid (1135), the quantity of which, however, appears to diminish in proportion as the oleic acid has become more oxidized. Oleic is metameric with ricinoleic acid.

Oleic acid forms two classes of salts, normal and acid. The normal salts of the alkalies are the only soluble ones. They form soaps, and by the evaporation of their aqueous solution they may be obtained in the condition of an amorphous mass. Oleate of potash forms a soft soap, which is the chief ingredient in Naples soap. Oleate of soda is a hard soap, and enters largely into the composition of Marseilles soap. The acid oleates of the alkalies are liquid and insoluble. The metallic oleates, such as those of copper and lead, are soluble in cold anhydrous alcohol, and in ether; they are thus separable from the stearates and palmitates, which are insoluble in these liquids.

(1127) *Action of Peroxide of Nitrogen and of Nitric Acid on Oleic Acid.*—Oleic acid by exposure to peroxide of nitrogen becomes converted into a solid fatty acid, isomeric with oleic acid, which has been called *elaidic acid*. In effecting this change an excess of the peroxide must be avoided, and the mass must be kept cool. The cause of this remarkable change is unknown. A small quantity of ammonia is formed during the reaction, as well as a portion of a neutral oily body. The quantity of peroxide of nitrogen required is very small, not exceeding $\frac{1}{300}$th of the weight of the oleic acid (1051).

Elaidic acid fuses at about 113°; it is very soluble in alcohol, from which it is deposited in beautiful pearly scales; it is less soluble in ether. Elaidic acid may be distilled in great part without alteration; but when fused with hydrate of potash it yields palmitic and acetic acid, like oleic acid.

When oleic acid is subjected in a capacious retort to the action of a large excess of nitric acid of sp. gr. 1·42 diluted with an equal bulk of water, it gradually disappears, producing a copious evolution of nitrous fumes, attended with a violent reaction. The results of the decomposition are very complicated, but the products obtained by this method of oxidizing oleic acid present considerable interest, since they contain, according to Redtenbacher, all the terms of the homologous series of the volatile acids ($C_{2n}H_{2n}O_4$) from the acetic to the capric acid inclusive, these acids being found in the distillate; whilst five or six fixed acids are left in the retort, and these form contiguous terms of a group of homologous dibasic acids of the formula $2\ HO,(C_{2n}H_{2n-4})O_6$. The quantity of the volatile acids is greater when the nitric acid used is very concentrated; if it be more dilute, that of the fixed acids is increased. The fixed acids which remain in the retort, are the following :—

Anchoic (Lepargylic) acid . .	$2\ HO,C_{18}H_{14}O_6$
Suberic acid	$2\ HO,C_{16}H_{12}O_6$
Pimelic acid	$2\ HO,C_{14}H_{10}O_6$
Adipic acid	$2\ HO,C_{12}H_8\ O_6$
Lipic acid	$2\ HO,C_{10}H_6\ O_6$
Succinic acid	$2\ HO,C_8H_4\ O_6$

It is interesting to remark that another acid of this group—viz., the sebacic acid ($2\ HO,C_{20}H_{16}O_6$) is a characteristic product of the distillation of oleic acid. Some of the acids of this series will now be described.

(*c*) *Dibasic Acids of the Oxalic Series* ($2\ HO,C_{2n}H_{2n-4}O_6$).

(1128) All the acids belonging to this series possess a considerable volatility, and may be partially sublimed without undergoing decomposition: they are soluble to a large extent in boiling water as well as in alcohol: they are likewise soluble in ether, and may be obtained in crystals without difficulty: some of them, like oxalic acid, crystallize with 4 Aq. Oxalic acid forms the lowest term in this group, and sebacic the highest which is at present known. The following table contains the names of the acids which have been ascertained to belong to this series :—

Acids.	Formulæ.	Fusing point.	Appearance.
Oxalic .	$2\ HO,C_4\ \ O_6$	Sublimes before fusing.	4-sided prisms with 4 Aq.
Malonic .	$2\ HO,C_6\ H_2\ O_8$	284°	Rhombohedral crystals.
Succinic .	$2\ HO,C_8\ H_4\ O_6$	356°	Four-sided prisms.
Lipic . .	$2\ HO,C_{10}H_6\ O_6$	about 290°	Rhombic prisms, very soluble.
Adipic .	$2\ HO,C_{12}H_8\ O_6$	266°	Radiated tufts.
Pimelic .	$2\ HO,C_{14}H_{10}O_6$	237°	Hard granular crystals.
Suberic .	$2\ HO,C_{16}H_{12}O_6$	257°	White crystalline powder.
Anchoic .	$2\ HO,C_{18}H_{14}O_6$	239°	
Sebacic .	$2\ HO,C_{20}H_{16}O_6$	260°	Thin pearly plates.

The acids of this group stand in the same relation to the diatomic alcohols that those of the acetic group do to the monatomic alcohols, glycol being converted by gradual oxidation into oxalic acid, as ordinary alcohol is into acetic acid. The lactic acid series appears to constitute an intermediate group of acids, the formation of which occurs during the process of oxidation of the glycols or diatomic alcohols. Thus, for example, glycol, by the absorption of 4 atoms of oxygen and the elimination of 2 of water, furnishes glycolic acid, and this acid, by the further absorption of 4 of oxygen and the elimination of 2 of water, furnishes oxalic acid. By a similar action of oxygen and separation of water we have the following compounds:—

$$\begin{matrix}\text{Diatomic}\\\text{alcohol}\end{matrix} + O_4 - H_2O_2 = \begin{matrix}\text{Lactic}\\\text{series.}\end{matrix} + O_4 - H_2O_2 = \begin{matrix}\text{Oxalic}\\\text{series.}\end{matrix}$$

$$\overbrace{C_4H_6\,O_4}^{\text{Ethyl-glycol.}} \qquad \overbrace{HO,C_4H_3O_5}^{\text{Glycolic acid.}} \qquad 2\,\overbrace{HO,C_4\quad O_6}^{\text{Oxalic acid.}};$$

$$\overbrace{C_6H_8\,O_4}^{\text{Trityl-glycol.}} \qquad \overbrace{HO,C_6H_5O_5}^{\text{Lactic acid.}} \qquad 2\,\overbrace{HO,C_6H_2O_6}^{\text{Malonic acid.}};$$

$$\overbrace{C_8H_{10}O_4}^{\text{Tetryl-glycol.}} \qquad \overbrace{HO,C_8H_7O_5}^{\text{Acetonic acid.}} \qquad 2\,\overbrace{HO,C_8H_4O_6}^{\text{Succinic acid.}}.$$

The glycolic series of acids upon this view must be regarded as monobasic, though diatomic (1089).*

Oxalic acid has been already described, Part II. p. 262.

(1129) *Malonic Acid* ($2\,HO,C_6H_2O_6 = 18 + 86$).—This acid, according to Dessaignes (*Liebig's Annal.* cvii. 251) may be obtained by the oxidation of malic acid. To a cold, dilute solution of malic acid, small quantities of solid bichromate of potash are to be gradually added until a quantity of the salt about equal in weight to the malic acid has been used. The liquid is diluted, and the reduced oxide of chromium separated by the addition of an excess of milk of lime. The greenish filtrate is mixed with acetate of lead, and the mixed precipitate of malonate and chromate of lead is mixed with nitric acid in quantity sufficient to decompose the organic salt. The filtrate is mixed with about three-fourths of the quantity of ammonia necessary to neutralize it, and the malonate of lead which is thrown down is washed, suspended in water, and decomposed by a current of sulphuretted hydrogen gas. On evaporating the filtrate, crystals of malonic acid are formed in a greenish syrupy liquid which contains malic acid and a little oxide of chromium. The crystals are drained and recrystallized. The acid forms large rhombohedral crystals which split readily into laminæ. It is freely soluble in water and in alcohol, has a sour taste, at 284° it melts, and at 302° it is partly sublimed unaltered, and partly converted into a mixture of carbonic and acetic acids:—

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* An interesting acid, the *glyoxalic*, discovered by Debus (*Phil. Mag.*, Nov., 1856), is probably the type of a group connecting the glycolic with the oxalic series. It is procured by the gradual decomposition of nitrous ether by means of water. The acid liquid obtained thus is evaporated in quantities not exceeding an ounce at a time over the water-bath, till of the consistence of syrup, when a mixture of glycolic, oxalic, and glyoxalic acid with the aldehyd of glycol (glyoxal) remains. It is neutralized with carbonate of lime and the liquid is mixed with an equal bulk of alcohol. The lime salts are precipitated, and glyoxal ($C_4H_2O_4$) is retained in solution. The precipitate is pressed and treated with boiling water, which on cooling deposits small, hard prisms of glyoxalate of lime ($CaO,C_4HO_5 + 2\,Aq$), while a double salt of glycolate and glyoxalate of lime remains in the mother liquor. Glyoxalic acid ($C_4H_2O_6$) may be obtained from the glyoxalate of lime by the cautious addition of oxalic acid, and by evaporation may be procured in the form of a deliquescent syrupy liquid, which may be volatilized almost without residue by heat, with the emission of white fumes. It is metameric with formic anhydride, and it is probably diatomic. A characteristic reaction of glyoxalic acid is the formation with lime of two salts, one of which is soluble and crystallizes in hard prisms, whilst the second, which is procured by the addition of lime water to the solution of the first, is nearly insoluble, but the latter salt speedily undergoes spontaneous decomposition, and a mixture of water and of oxalate and glycolate of lime is the result. The same change takes place still

$$\overbrace{C_6H_4O_8}^{\text{Malonic acid.}} = \overbrace{C_4H_4O_4}^{\text{Acetic acid.}} + \overbrace{C_2O_4}^{\text{Carb. acid.}}.$$

Malonates.—The salts of malonic acid with the alkalies are soluble, their solutions give white precipitates with the solutions of salts of lime, baryta, lead, mercury, and silver, but none with salts of iron. The salts of suboxide of mercury give a white precipitate, which blackens if the liquid be boiled. The malonates of potash and ammonia are deliquescent, but crystallizable; the baryta salt forms sparingly soluble silky tufts; the lime salt furnishes small transparent needles; the silver salt falls as a crystalline powder.

The malonic resembles oxalic acid more than it does the succinic.

(1130) *Succinic Acid* ($2\ HO,C_8H_4O_6 = 18 + 100$).—This acid, as its name implies, was originally obtained from amber (*succinum*),

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more rapidly if the lime water be in slight excess and the liquid is boiled; the decomposition is shown by the equation:—

$$\overbrace{2\,(CaO,C_4HO_5,2\,HO)}^{\text{Glyoxalate of lime.}} + CaO,HO, = 2\,\overbrace{CaO,C_4O_6}^{\text{Oxalate of lime.}} + \overbrace{CaO,C_4H_3O_5}^{\text{Glycolate of lime.}} + 2\,H_2O_2.$$

The soluble glyoxalates give a white crystalline precipitate with acetate of lead, soluble in acetic acid, but no precipitate with either nitrate of silver, nitrate of baryta, or chloride of copper. It is probable that glyoxalic acid is the type of a class of similar substances, the general formula of which is, $C_{2n}H_{2n-2}O_6$.

in which it exists ready formed. When amber is submitted to destructive distillation, a quantity of succinic acid passes over amongst other substances. It is, however, easily obtained artificially, by acting upon stearic or palmitic acid with nitric acid. Succinic acid also occurs in the leaves of the wormwood and in the resins of many of the pine tribe. It may likewise be obtained, by fermentation, from asparagin, and from malic acid (Dessaignes), malate of lime yielding nearly one-third of its weight of it. In order to procure it from malic acid, 3 lb. of crude malate of lime are to be diffused through a gallon of warm water, and four ounces of decayed cheese are to be added to the mixture, which is to be kept at a temperature of 100° for about a week. Carbonic acid is disengaged, whilst a mixture of crystallized carbonate and succinate of lime is deposited, and acetate of lime remains in solution (1140).

$$\overbrace{6\,(2\,CaO,C_8H_4O_8)}^{\text{Malate of lime.}} = \overbrace{4(2\,CaO,C_8H_4O_6)}^{\text{Succinate of lime.}} + \overbrace{2\,(CaO,C_4H_3O_3)}^{\text{Acetate of lime.}} + 2\,CaO,C_2O_4 + 3\,C_2O_4 + H_2O_2.$$

The deposited succinate of lime is to be collected upon a linen filter and washed with cold water, after which it may be decomposed by hydrochloric acid, and the succinic acid purified by crystallization. The decomposition, however, is not always so simple as is represented in the foregoing equation. The formation of lactate of lime has often been observed to accompany the transformation of malic into succinic acid, and it frequently happens, particularly if the temperature be at all high, that a quantity of hydrogen is disengaged during the fermentation: when this occurs it indicates the formation of butyric acid, which is also accompanied by a small quantity of an essential oil with an agreeable odour of apples. The relation of malic to lactic acid is very simple:—

$$\overbrace{2\,HO,C_8H_4O_8}^{\text{Malic acid.}} = \overbrace{HO,C_6H_5O_5}^{\text{Lactic acid.}} + C_2O_4;$$

and the presence of lactic acid readily accounts for the formation of butyric acid (1138). An interesting relation also exists between butyric and succinic acids; butyric acid when treated with nitric acid being convertible by oxidation into the succinic:—

$$\overbrace{2\,(HO,C_8H_7O_3)}^{\text{Butyric acid.}} + 3\,O_4 = \overbrace{2\,(2\,HO,C_8H_4O_6)}^{\text{Succinic acid.}} + 2\,H_2O_2.$$

Succinic acid crystallizes in large, regular rhombic tables, which require five parts of cold and two of boiling water for solution. Alcohol dissolves it freely, but it is only sparingly soluble in ether. Succinic acid melts at a temperature of from 347° to 356°, but if suddenly heated to 455° it melts, boils, and sublimes completely. During the sublimation the acid loses a portion of its water, and if distilled with anhydrous phosphoric acid the anhydride ($C_8H_4O_6$) may be obtained without difficulty. Succinic anhydride is soluble in alcohol and in water; its aqueous solution rapidly becomes converted into the ordinary hydrated acid.

Succinic acid is a very stable compound. It may be boiled for many hours with strong nitric acid without undergoing decomposition, and its aqueous solution is not affected by chlorine, or by a mixture of chlorate of potash and hydrochloric acid. Succinic acid forms two classes of salts, normal and acid, but with potash it yields three salts:—a normal deliquescent salt ($2\ KO,C_8H_4O_6 + 4\ Aq$); an acid salt ($KO,HO,C_8H_4O_6 + 4\ Aq$; Döpping), which crystallizes in transparent efflorescent six-sided prisms, soluble in alcohol; and a remarkable superacid salt ($KO,\ 3\ HO,\ 2\ C_8H_4O_6 + 2\ Aq$), corresponding to the quadroxalate of potash; this salt may be deprived of 3 equivalents of water by raising its temperature to 212° (Fehling). *Succinate of soda* ($2\ NaO,C_8H_4O_6 + 12\ Aq$) crystallizes in transparent rhomboidal prisms. *Succinate of ammonia* ($2\ H_4NO,\ C_8H_4O_6$) is sometimes employed to separate iron in perfectly neutral solutions from salts of nickel, cobalt, and manganese. *Succinate of magnesia and potash* ($MgO,KO,C_8H_4O_6 + 5\ Aq$) may be obtained in double six-sided pyramids, by allowing the two salts mixed in equivalent proportions to crystallize together. Succinic acid forms several nearly insoluble compounds with oxide of *lead;* the normal salt ($2\ PbO,C_8H_4O_6$) is white and crystalline; another compound, ($3\ PbO,C_8H_4O_6$), is fusible in warm water; and if either of the foregoing precipitates be digested with ammonia, a compound may be obtained with a still larger proportion of base.

The succinates are characterized by the bulky brown precipitate of persuccinate of iron which they yield in neutral solutions of salts of the sesquioxide of iron.

Succinic acid combines readily with sulphuric anhydride, and forms a deliquescent crystallizable compound acid, termed *succino-sulphuric acid* ($3\ HO,C_8H_3O_5,S_2O_6 + 2\ Aq$), which requires 3 equivalents of base for its saturation.

(1131) When succinic anhydride is distilled with an equivalent quantity of perchloride of phosphorus, oxychloride of phosphorus passes over at first; and at a more elevated temperature *succinic oxychloride* ($C_8H_4O_4Cl_2$) is obtained. This compound not identical, with the acetonic; but the lactic is an impo and interesting acid.

(1138) **Lactic Acid** ($HO,C_6H_5O_5=9+81$).—The cir stances most favourable to the production of this acid already been mentioned (969). It is best obtained by dis ing 8 parts of cane sugar in about 50 parts of water; to solution 1 part of casein, or of poor cheese, and 3 part chalk must be added: if this mixture be set aside for two or weeks, and maintained at a temperature of 80°, it grad becomes filled with a mass of crystals of lactate of lime. T crystals must be purified by re-crystallization, and treated about one third of their weight, or their exact chemical equiva of sulphuric acid; the residue must then be digested in alc which leaves the sulphate of lime and dissolves the lactic pure lactic acid remains on evaporating the solution.

Pasteur considers that a specific ferment is concerned in production of the lactic fermentation. During the ferment of the mixture of sugar and casein with chalk, a layer of part of a grey substance is observed upon the surface of the sedim This substance may be obtained free from admixture by dige washed yeast in 15 or 20 times its weight of boiling water, solving 1 part of sugar in 20 of the filtered liquid, adding and then a very small quantity of the grey deposit above tioned, taken from a portion of liquid in the active stage of fermentation. The acid fermentation rapidly sets in, the disappears, and the grey sediment is gradually deposited in siderable quantity: a solution of any nitrogenous substance in this case be substituted for the infusion of beer yeast. ferment thus obtained, when examined by the microscope, is se consist of little globules, or very short articulations, either iso or in threads, constituting irregular flocculent particles, smaller than those of beer yeast, and exhibiting a rapid gyr motion. When washed with a large quantity of pure wate then diffused through a solution of pure sugar, acidification mences immediately, and proceeds gradually until arrested by excess of free acid. The formation of lactic acid is always ac panied by the development of small quantities of butyric alcohol, mannite, and a viscous substance,—the proportions of bodies varying greatly in different experiments. When the is kept neutral by the addition of chalk, little or no mannit gum are formed.

Lactic acid is also formed in a variety of other processes Wurtz has recently obtained it by the gradual oxidation of ulé by digesting succinic acid in a sealed tube for some urs at a temperature of 356°, with bromine and a considerable portion of water. It is freely soluble in water, and crystallizes h greater difficulty than dibromosuccinic acid. When an ous solution of this acid is boiled with oxide of silver, bromide silver is formed, and malate of silver is obtained :—

$$2\,\overbrace{HO,C_8H_3BrO_6}^{\text{Monobromosuccinic acid.}}+3\,AgO=2\,\overbrace{AgO,C_8H_4O_8}^{\text{Malic acid.}}+AgBr.$$

The reconversion of tartaric and malic into succinic acid may be effected by heating them with hydriodic acid in a sealed e for some hours. Iodine is liberated and succinic acid crysizes on evaporating the solution :—

$$2\,\overbrace{HO,C_8H_4O_8}^{\text{Malic acid.}}+2\,HI=2\,\overbrace{HO,C_8H_4O_6}^{\text{Succinic acid.}}+\ H_2O_2+\ I_2;$$

$$2\,\overbrace{HO,C_8H_4O_{10}}^{\text{Tartaric acid.}}+4\,HI=2\,\overbrace{HO,C_8H_4O_6}^{\text{Succinic acid.}}+2\,H_2O_2+2\,I_2.$$

The three next terms of the series—viz., the lipic, adipic, and elic acids, are unimportant: they are formed along with suberic during the oxidation of oleic by nitric acid; these acids may crystallized without difficulty.

(1133) *Suberic Acid* (2 $HO,C_{16}H_{12}O_6$).—This compound was inally observed among the products of the oxidation of cork itric acid, and hence it derives its name (from *suber*, cork). k, however, yields it in but very small quantity, and even that ntity is probably owing to the presence of a small proportion xy matter. The acid is a rather frequent product of the oxiion of the fats, and particularly of the acids of the stearic series. s easily obtained by boiling stearic acid with nitric acid for e days; upon concentrating the liquid it deposits crystals of ric acid, mixed with a large quantity of succinic acid. The er acid is easily removed by washing with cold water, and the ringly soluble suberic acid is purified by crystallization from ing water. It forms a white crystalline powder, destitute of r, but having a slightly acid taste, and feebly reddening litmus r. It requires about 100 times its weight of cold water for on, but only twice its weight of boiling water. It is also ble in alcohol and in ether. When heated it fuses at about nd creeps up the side of the vessel in which it is heated, oing a sort of spurious sublimation at a high temperature. berates of the alkalies and of the earths are soluble and zable; they yield with salts of lead, silver, and zinc, white soluble *precipitates.*

(1134) *Anchoic* or *Lepargylic Acid* ($HO,C_{18}H_{14}O_6$) was found by Buckton among the products of the oxidation of Chinese wax, and by Wirz among those of cocoa-nut oil by a similar process. It crystallizes in white warty masses, fuses at about 239°, and is freely soluble in boiling water. Its vapours have a peculiarly irritating effect upon the organs of respiration.

(1135) *Sebacic Acid* ($2\ HO, C_{20}H_{16}O_6$).—This acid is easily obtained by the distillation of oleic acid, and most of the fixed oils also yield it by distillation, owing to the decomposition of the olein which they contain: the acid is accompanied in this operation by various hydrocarbons, and by other volatile acids. It may likewise be readily obtained in large quantity from the fixed residue of the distillation of castor oil with hydrate of potash; ricinoleic acid yielding octylic (caprylic) alcohol, sebacic acid, and free hydrogen:—

$$\overbrace{HO,C_{36}H_{33}O_5}^{\text{Ricinoleic acid.}} + 2\,(KO,HO) = \overbrace{C_{16}H_{17}O,HO}^{\text{Octylic alcohol.}} + 2\,\overbrace{KO,C_{20}H_{16}O_6}^{\text{Sebate of potash.}} + 2\ H.$$

The sebate of potash is dissolved in boiling water and decomposed by the addition of hydrochloric acid; sebacic acid crystallizes in needles as the liquid cools. This acid is easily recognised by its ready solubility in boiling water, from which it crystallizes in pearly scales, as it is nearly insoluble at ordinary temperatures. It fuses at 260°, and may be sublimed without decomposition, becoming condensed in needles which resemble those of benzoic acid. Its vapours have a greasy odour, and produce a very irritating effect upon the lungs. Sebacic acid is very soluble in alcohol and in ether. By oxidation with nitric acid it yields a mixture of lipic and succinic acids, mistaken by Schlieper for pyrotartaric acid.

Sebacic acid forms both normal and acid salts. The sebates of the alkalies and of the earths are soluble, but the other sebates are nearly insoluble.

(*d*) *Acids of the Glycolic Series.* ($C_{2n}H_{2n}O_6$).

(1136) Intermediate between the acetic and the oxalic series of acids is one which may be described as the glycolic series.

$$\overbrace{C_{2n}H_{2n}O_4}^{\text{Acetic.}} \quad ; \quad \overbrace{C_{2n}H_{2n}O_6}^{\text{Glycolic.}} \quad ; \quad \overbrace{C_{2n}H_{2n-2}O_8}^{\text{Oxalic.}}.$$

It includes the following terms:—

es the properties of the ordinary

lbumen; when present in small quan-
lk in the cold, but does so if gently
en heated with sulphuric acid, give off
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acid the lactic is converted into oxalic

acid are not very definite. The best mode
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liquid suspected to contain it, to the consis-
over a water-bath, treating the residue with
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thus separated in combination with the oxalic acid,
d and the excess of oxalic acid remain dissolved.
d is carefully neutralized by baryta water, which
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dissolved. The lactate of baryta may be decom-
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(1138) Lactic Acid ($HO,C_6H_5O_5=9+81$).—The circumstances most favourable to the production of this acid have already been mentioned (969). It is best obtained by dissolving 8 parts of cane sugar in about 50 parts of water; to this solution 1 part of casein, or of poor cheese, and 3 parts of chalk must be added: if this mixture be set aside for two or three weeks, and maintained at a temperature of 80°, it gradually becomes filled with a mass of crystals of lactate of lime. These crystals must be purified by re-crystallization, and treated with about one third of their weight, or their exact chemical equivalent, of sulphuric acid; the residue must then be digested in alcohol, which leaves the sulphate of lime and dissolves the lactic acid: pure lactic acid remains on evaporating the solution.

Pasteur considers that a specific ferment is concerned in the production of the lactic fermentation. During the fermentation of the mixture of sugar and casein with chalk, a layer of particles of a grey substance is observed upon the surface of the sediment. This substance may be obtained free from admixture by digesting washed yeast in 15 or 20 times its weight of boiling water, dissolving 1 part of sugar in 20 of the filtered liquid, adding chalk, and then a very small quantity of the grey deposit above mentioned, taken from a portion of liquid in the active stage of lactic fermentation. The acid fermentation rapidly sets in, the chalk disappears, and the grey sediment is gradually deposited in considerable quantity: a solution of any nitrogenous substance may in this case be substituted for the infusion of beer yeast. The ferment thus obtained, when examined by the microscope, is seen to consist of little globules, or very short articulations, either isolated or in threads, constituting irregular flocculent particles, much smaller than those of beer yeast, and exhibiting a rapid gyratory motion. When washed with a large quantity of pure water and then diffused through a solution of pure sugar, acidification commences immediately, and proceeds gradually until arrested by the excess of free acid. The formation of lactic acid is always accompanied by the development of small quantities of butyric acid, alcohol, mannite, and a viscous substance,—the proportions of these bodies varying greatly in different experiments. When the liquid is kept neutral by the addition of chalk, little or no mannite and gum are formed.

Lactic acid is also formed in a variety of other processes: thus Wurtz has recently obtained it by the gradual oxidation of pro-en redissolved in water possesses the properties of the ordinary iety β.

Lactic acid coagulates albumen; when present in small quan- it does not curdle milk in the cold, but does so if gently ed. The lactates, when heated with sulphuric acid, give off y carbonic oxide, and deposit a solid brown matter resembling ic acid. By nitric acid the lactic is converted into oxalic .

The tests for lactic acid are not very definite. The best mode dentifying it (whether it be free or in combination), consists vaporating the liquid suspected to contain it, to the consis- e of a syrup over a water-bath, treating the residue with hol, and adding a small quantity of a solution of oxalic acid: bases are thus separated in combination with the oxalic acid, the lactic acid and the excess of oxalic acid remain dissolved. acid liquid is carefully neutralized by baryta water, which es a precipitate of oxalate of baryta, whilst the lactate of this remains dissolved. The lactate of baryta may be decom- d by adding a solution of sulphate of lime; sulphate of baryta us separated, and the lactate of lime may be crystallized from alcoholic solution, and the form of the crystals ascertained he microscope.

When anhydrous lactate of lime is distilled with twice its ht of perchloride of phosphorus, it yields a colourless body, h Wurtz termed *chlorlactyl* ($C_6H_4O_2Cl_2$), the oxychloride of c acid; and this substance, when decomposed by water and led, yields chloropropionic acid, from which propionic acid is y obtained (1113).

Lantemann has also succeeded in converting lactic acid into onic, by saturating the lactic with hydriodic acid, keeping mixture cool, then sealing it in a tube, and heating it to for some time. Iodine is liberated and propionic acid is ed:—

$$\overbrace{HO,C_6H_5O_5}^{\text{Lactic acid.}} + 2\,HI = \overbrace{HO,C_6H_5O_3}^{\text{Propionic acid.}} + I_2 + H_2O_2.$$

eduction is effected still more easily by distilling 3·5 parts tic acid with 4 of biniodide of phosphorus, when propionic asses over, coloured with a little free iodine.

f leucic acid comparatively little is known. It is a pro- f the decomposition of leucine (1427).

passes at once into hydrated lactic acid, by assuming 2 atoms of water. Lactide readily absorbs ammonia, and is converted into lactamide; $C_6H_4O_4 + H_3N = (H_2N)C_6H_5O_4$; this body is isomeric with sarkosine, and with alanine.

Lactates.—The lactic was regarded by Gerhardt as a dibasic acid, and he accordingly doubled its formula, representing it as $C_{12}H_{12}O_{12}$; but the researches of Wurtz and of Kolbe seem to indicate that the older and simpler formula given above is to be preferred. The lactates are soluble in water, but insoluble in ether, and nearly so in cold alcohol: those of the alkalies do not crystallize. Neutral and acid lactates may be formed with lime and with baryta. *Bilactate of baryta* ($BaO,HO, 2\ C_6H_5O_5$) may be crystallized: the neutral lactate is very soluble in water, and does not crystallize. *Acid lactate of lime* ($CaO,HO, 2\ C_6H_5O_5 + Aq$) crystallizes in radiated needles. *Normal lactate of lime* crystallizes in tufts of prisms, with 5 Aq. The *lactate of zinc*, ($ZnO, C_6H_5O_5 + 3\ Aq$) is one of the most characteristic salts of this acid; it crystallizes in crusts, consisting of four-sided prisms, which are sparingly soluble. *Lactate of copper* ($CuO,C_6H_5O_5 + 2\ Aq$) is only incompletely precipitated by hydrate of potash, an excess of which gives with it a deep blue solution; but the whole of the oxide of copper is separated on the addition of an excess of hydrate of lime. A *sublactate* of copper ($2\ CuO,C_6H_5O_5$) may also be obtained. Several other basic lactates may be formed, which, like sublactate of copper, contain 2 equivalents of base.

The variety of lactic acid which is obtained from the juice of flesh, yields salts which crystallize with a proportion of water differing from that contained in the salts furnished by the ordinary acid. The *sarkolactic* acid from muscular tissue may be distinguished as the variety α; its salts crystallize with smaller proportions of water of crystallization than those of the ordinary form of the acid, which may be distinguished as the variety β; thus it gives a salt of zinc, which contains only 2 Aq, and crystallizes in slender needles; it begins to undergo decomposition below 300°, whilst the salt of the ordinary acid may be heated to 400° without experiencing any decomposition. The neutral salt of lime, of the variety α, also crystallizes with 4 Aq, and is less soluble than the variety β, which crystallizes with 5 Aq. Similar differences are observed in the copper salts; but the copper salt α is much the more soluble of the two.

Strecker finds that the sarkolactic acid, when separated from its zinc salt by sulphuretted hydrogen, and heated to between 266° and 284°, is gradually converted into lactic anhydride, and this when redissolved in water possesses the properties of the ordinary variety β.

Lactic acid coagulates albumen; when present in small quantity it does not curdle milk in the cold, but does so if gently heated. The lactates, when heated with sulphuric acid, give off pure carbonic oxide, and deposit a solid brown matter resembling ulmic acid. By nitric acid the lactic is converted into oxalic acid.

The tests for lactic acid are not very definite. The best mode of identifying it (whether it be free or in combination), consists in evaporating the liquid suspected to contain it, to the consistence of a syrup over a water-bath, treating the residue with alcohol, and adding a small quantity of a solution of oxalic acid: the bases are thus separated in combination with the oxalic acid, but the lactic acid and the excess of oxalic acid remain dissolved. The acid liquid is carefully neutralized by baryta water, which causes a precipitate of oxalate of baryta, whilst the lactate of this base remains dissolved. The lactate of baryta may be decomposed by adding a solution of sulphate of lime; sulphate of baryta is thus separated, and the lactate of lime may be crystallized from the alcoholic solution, and the form of the crystals ascertained by the microscope.

When anhydrous lactate of lime is distilled with twice its weight of perchloride of phosphorus, it yields a colourless body, which Wurtz termed *chlorlactyl* ($C_6H_4O_2Cl_2$), the oxychloride of lactic acid; and this substance, when decomposed by water and distilled, yields chloropropionic acid, from which propionic acid is easily obtained (1113).

Lautemann has also succeeded in converting lactic acid into propionic, by saturating the lactic with hydriodic acid, keeping the mixture cool, then sealing it in a tube, and heating it to 284° for some time. Iodine is liberated and propionic acid is formed:—

$$\overbrace{HO,C_6H_5O_5}^{\text{Lactic acid.}} + 2\ HI = \overbrace{HO,C_6H_5O_3}^{\text{Propionic acid.}} + I_2 + H_2O_2.$$

This reduction is effected still more easily by distilling 3·5 parts of lactic acid with 4 of biniodide of phosphorus, when propionic acid passes over, coloured with a little free iodine.

Of leucic acid comparatively little is known. It is a product of the decomposition of leucine (1427).

§ IV. CERTAIN POLYBASIC VEGETABLE ACIDS.

(1139) Several polybasic acids, some of which, such as the malic, tartaric, and citric, are very extensively diffused through the vegetable kingdom, may conveniently be considered in juxtaposition with the fatty acids; as a very close connexion has recently been shown to exist between malic and tartaric acid and the succinic, a member of the oxalic acid group.

The acids which will now be described are the following:—

1. Malic acid . . .	$2\,HO,C_8\,H_4\,O_8$
2. Tartaric acid . . .	$2\,HO,C_8\,H_4\,O_{10}$
3. Citric acid . . .	$3\,HO,C_{12}H_5\,O_{11}+2\,Aq$
4. Meconic acid . . .	$3\,HO,C_{14}H\ O_{11}+6\,Aq$
5. Gallotannic acid . .	$2\,HO,C_{54}H_{20}O_{32}$
6. Gallic acid . .	$3\,HO,C_{14}H_3\,O_7\ +2\,Aq$
7. Quinic acid . . .	$2\,HO,C_{28}H_{20}O_{20}$
8 and 9. Sorbic and Parasorbic acids	$HO,C_{12}H_7\,O_3$

1. *Malic Acid, and its Derivatives.*

(1140) MALIC ACID ($2\,HO,C_8H_4O_8=18+116$).—This acid is extensively diffused through the vegetable kingdom; it occurs abundantly in most acidulous fruits, particularly in unripe apples, gooseberries, and currants, in which it is accompanied by citric acid. The footstalks of the garden rhubarb also contain it in considerable quantity, mixed with oxalic and phosphoric acids, and they furnish a convenient source of malic acid; but it is usually extracted from the unripe berries of the mountain ash. The dried leaves of the tobacco plant are also rich in bimalate of lime.

In order to obtain the acid, the expressed juice either of the mountain ash berries or of the leafstalks of the rhubarb, is nearly neutralized with milk of lime, and a certain quantity of chloride of calcium is added in order to decompose the malate of potash which always accompanies the free acid. A precipitate is thus formed which contains the citric, phosphoric, and tartaric acids in combination with lime. The liquid must be left with a feebly acid reaction, in order to avoid the subsequent precipitation of the colouring matter. The clear solution is then to be filtered, and the filtrate boiled for several hours: neutral malate of lime is thus gradually separated in the form of an insoluble powder. After this precipitate has been washed with cold water, it is to be added in small portions at a time, so long as it continues to be dissolved, to hot dilute nitric acid (containing one part of acid to ten of water). The liquid thus obtained is to be filtered, and set aside to crystallize: well-defined crystals of bimalate of lime are then deposited. The bimalate obtained in this way may be purified by treating it with animal charcoal and recrystallizing it from water. Its solution may afterwards be converted into malate of lead by the addition of acetate of lead, and the malate of lead when decomposed with sulphuric acid, yields free malic acid, from which the last traces of lead may be removed by means of sulphuretted hydrogen.

Properties.—The aqueous solution of malic acid, when evaporated to the consistence of syrup and left in a warm place, gradually deposits radiated masses composed of brilliant four or six-sided prisms. They are deliquescent in a moist air, and are soluble in alcohol; when heated they undergo fusion below 212°. Malic acid has a very sour taste; its solution, unless quite pure, becomes mouldy and viscid when kept.

Malic acid, when heated to 350°, is decomposed, water is expelled, and two isomeric acids, the *malæic* and the *fumaric*, are formed, and at the same time malæic anhydride is obtained:—

$$2\,(\overbrace{2\,HO,C_8H_4O_8}^{\text{Malic acid.}}) = 2\,H_2O_2 + 2\,\overbrace{HO,C_8H_2O_6}^{\text{Malæic acid.}} + 2\,\overbrace{HO,C_8H_2O_6}^{\text{Fumaric acid.}}.$$

Hydrated malæic acid when maintained in a state of fusion at 300°, is converted into a crystalline mass of fumaric acid. If distilled by a temperature suddenly elevated to 460°, malæic anhydride is formed. Sulphuric acid, when heated with malic acid, decomposes it and liberates carbonic oxide. Nitric acid converts it first into fumaric and then into oxalic acid. When heated with hydrochloric acid, malic acid is gradually converted into fumaric acid.

Kekulé (*Liebig's Annal.* Suppl. 1861, 131) has shown that both fumaric acid and its isomeride, malæic acid, combine directly with bromine, and furnish crystals of dibromosuccinic acid: and further, if fumaric acid be dissolved in water, and digested with an amalgam of sodium, the nascent hydrogen combines with the acid and converts it into succinic acid:—

$$\overbrace{C_8H_4O_8}^{\text{Fumaric acid.}} + Br_2 = \overbrace{C_8H_4Br_2O_8}^{\text{Dibromosuccinic acid.}};$$

$$C_8H_4O_8 + H_2 = \overbrace{C_8H_6O_8}^{\text{Succinic acid.}}.$$

From the dibromosuccinic, tartaric acid (inactive) was obtained.

Malic acid may also be converted into succinic acid by heating it in sealed tubes with hydriodic acid; whilst iodine is liberated (Schmitt) :—

$$\overbrace{2\,HO,C_8H_4O_8}^{\text{Malic acid.}}+2\,HI=\overbrace{2\,HO,C_8H_4O_6}^{\text{Succinic acid.}}+I_2+H_2O_2;$$

and succinic acid may be reconverted into malic by first preparing bromosuccinic acid and decomposing it by oxide of silver (1132; Kekulé).

When malic acid is fused with hydrate of potash at a temperature of 300°, hydrogen is disengaged, and oxalate and acetate of potash are formed :—

$$\overbrace{2\,HO,C_8H_4O_8}^{\text{Malic acid.}}+3\,(KO,HO)=\overbrace{2\,KO,C_4O_6}^{\substack{\text{Oxalate}\\\text{of potash.}}}+\overbrace{KO,C_4H_3O_3}^{\substack{\text{Acetate}\\\text{of potash.}}}+2\,H_2O_2+H_2.$$

When a dilute solution of malic acid is gradually oxidized in the cold by the cautious addition of bichromate of potash, malonic acid ($2\,HO,C_6H_2O_6$) (the acid intermediate between the succinic and the oxalic) is amongst the products (1129).

(1141) *Malates.*—The malic is a dibasic acid,* and has a strong tendency to form acid salts. The bimalate of ammonia and the bimalate of lime are readily obtained in large regular crystals; but its most characteristic salt is the *malate of lead* ($2\,PbO,C_8H_4O_8+6\,Aq=339+54$), which when first precipitated is amorphous, but if left in the liquid, becomes converted into radiated tufts of silky needles. It is fusible into a pasty mass at a temperature below that of boiling water. Malic acid, like the tartaric, prevents the precipitation of iron from its solution by the alkalies. Malic acid gives no precipitate with lime-water, either when cold or hot; but, by evaporation of the liquid, a crystallized malate of lime is produced, which is dissolved by boiling water. These characters distinguish the malic from oxalic, tartaric, racemic, and citric acids. Most of the malates are soluble in water, but not in alcohol. Many of the malates, such as those of lime and baryta, when heated to 400°, lose two atoms of water, and become converted into fumarates, from which fumaric acid (identical with the acid of the *Fumaria officinalis*) may be obtained in characteristic broad, slender, sparingly soluble, striated prisms.

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* It is, however, probably formed upon the plan of three double atoms of water, and is consequently triatomic, though only two atoms of hydrogen admit of displacement by metals under ordinary circumstances, *e.g.* :—

$$\overbrace{\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_6}^{\text{Type.}};\quad\overbrace{\left.\begin{matrix}C_8H_3O_4\\H,H_2\end{matrix}\right\}O_6}^{\text{Malic acid.}};\quad\overbrace{\left.\begin{matrix}C_8H_3O_4\\H,2\,Ca\end{matrix}\right\}O_6}^{\text{Normal malate.}};\quad\overbrace{\left.\begin{matrix}C_8H_3O_4\\H,H\,Ca\end{matrix}\right\}O_6}^{\text{Acid malate.}}.$$

Bimalate of Ammonia ($H_4NO,HO,C_8H_4O_8$) is readily obtained by dividing a solution of malic acid into two equal portions, exactly neutralizing one with ammonia, and then adding to it the other portion of the acid; on evaporation, brilliant right rhombic prisms are formed. It is remarkable that the optically active bimalate of ammonia (1142) forms a crystallizable double salt with the dextrotartrate of ammonia, but it forms no such compound with the lævotartrate. Bimalate of ammonia, when submitted to distillation, is converted into a brick-coloured powder, termed *fumarimide*:—

$$\overbrace{H_4NO,HO,C_8H_4O_8}^{\text{Bimalate of ammonia.}} = \overbrace{C_8H_3NO_4}^{\text{Fumarimide.}} + 3\ H_2O_2.$$

Bimalate of Lime ($CaO,HO,C_8H_4O_8 + 8\ Aq = 153 + 72$).—This salt is obtained in beautiful transparent rhombic prisms, by dissolving the normal malate of lime in hot dilute nitric acid, and allowing the solution to cool. It is sparingly soluble in cold water.

The *normal malate of lime* exists in two modifications: one of these ($2\ CaO,C_8H_4O_8 + 4\ Aq = 172 + 36$) is readily soluble. It is obtained by neutralizing malic acid or the bimalate of lime with milk of lime; the solution may be evaporated at ordinary temperatures, and deposits large brilliant crystalline plates. If the solution of this salt be boiled for some hours, it gradually deposits a sparingly soluble, granular, crystalline powder, which when analysed is found to contain 2 Aq, but has in other respects the same composition as the soluble malate. The soluble form of malate of lime may also be obtained with 5 Aq and with 6 Aq. If malate of lime be placed beneath a layer of water, in a vessel loosely covered, it gradually undergoes decomposition: carbonic acid is disengaged, and a mixture of lactic, acetic, and succinic (1130) acids is formed. This change is accelerated by the addition of a small quantity of yeast, or of decaying cheese, to the mixture:—

$$3\,(2\ \overbrace{HO,C_8H_4O_8}^{\text{Malic acid.}}) = 2\,(2\ \overbrace{HO,C_8H_4O_6}^{\text{Succinic acid.}}) + \overbrace{HO,C_4H_3O_3}^{\text{Acetic acid.}} + 2\ C_2O_4 + H_2O_2.$$

If the fermentation be conducted at a higher temperature, hydrogen gas is evolved, and butyrate of lime is the principal product.

Malate of zinc ($2\ ZnO,C_8H_4O_8 + 6\ Aq$) is sparingly soluble in cold water, but is taken up by ten times its weight of boiling water; short, rectangular, brilliant, very hard prisms are deposited as it cools. A bimalate of zinc ($ZnO,HO,C_8H_4O_8 + 4\ Aq$) may also be obtained in octohedral crystals.

Besides the neutral malate of lead, a *basic malate* (4 PbO, $C_8H_4O_8$) may be obtained by precipitating a soluble malate by subacetate of lead ; it is not fusible in boiling water.

Malate of silver forms a white, anhydrous, insoluble powder.

(1142) *Metameric Modifications of Malic Acid.*—Malic acid has been ascertained by Pasteur to exist in two modifications, which may be distinguished by the letters α and β ; the variety α, which exerts a left-handed rotatory action upon a ray of polarized light, is the ordinary form of the acid ; some of its salts exert a rotation to the left, others to the right. The variety β is destitute of any such rotatory power, and hence is termed *inactive malic acid.* The latter modification of the acid presents scarcely any perceptible chemical difference from the acid α, but it crystallizes rather more readily from its aqueous solution, since it is somewhat less soluble and is not deliquescent: it also requires a temperature of 272° for its fusion: when heated a few degrees beyond this point it is decomposed, and furnishes the same compounds as the ordinary form of the acid. Inactive malic acid is procured by the action of nitrous acid upon inactive aspartic acid (1144); during this reaction nitrogen escapes in abundance, and if the acid liquid be supersaturated with ammonia when the disengagement of gas has ceased, the addition of a solution of acetate of lead causes the separation of a precipitate of inactive malate of lead; from this malate of lead sulphuretted hydrogen liberates the inactive acid, β.

It will be observed that the formula of malic acid differs from that of the tartaric, by containing two atoms less of oxygen.

(1143) *Amides of Malic Acid—Asparagin.*—Malic acid, like the dibasic acids in general, forms two amides ; one of these possesses the properties of an acid, and has been termed *malamic acid* ($HO,H_2N,C_8H_4O_7$), which is isomeric with aspartic acid, if not identical with it.

Asparagin ($C_8H_8N_2O_6 + 2$ Aq).—This crystalline body is extracted from the young shoots of the asparagus and of the climbing vetch, from the roots of the marshmallow, and from several other plants. It may generally be procured in crystals by simply evaporating the expressed juice of one of these plants. The brown crystals thus obtained may be purified by treatment with animal charcoal and re-crystallization. Asparagin, when pure, forms beautiful octohedra, or rhombic prisms, which are soluble in about 60 parts of cold water, and are freely dissolved by boiling water, by dilute acids and alkalies, and by proof spirit. It has a mawkish and cooling taste. When dissolved in water, or in ine solutions, it exerts a left-handed rotation upon a ray of ized light; but if dissolved in acids it produces a right-ed rotation of the ray. Asparagin is chiefly remarkable for facility with which it is decomposed into aspartic acid and onia, when its aqueous solution is heated with alkalies or h acids:—

$$\overbrace{C_8H_8N_2O_6,2\,HO}^{\text{Asparagin.}} = \overbrace{HO,C_8H_6NO_7}^{\text{Aspartic acid.}} + H_3N.$$

en an aqueous solution of asparagin is heated under pressure, wholly converted into aspartate of ammonia; and the same ct takes place slowly when the solution is exposed to a tempe-ure of 212° for a few days. At a moderate heat, asparagin es its 2 equivalents of water of crystallization, and in its anhy-us form is isomeric with malamide.

Piria found that if the expressed juice of the vetch were allowed utrefy, the asparagin which it contained was gradually converted succinate of ammonia, by the assimilation of 2 equivalents of rogen:—

$$\overbrace{C_8H_8N_2O_6,2\,HO}^{\text{Asparagin.}}+H_2= \overbrace{2\,H_4NO,C_8H_4O_6}^{\text{Succinate of ammonia.}}.$$

en asparagin is treated with nitric acid which has been satu-d with nitrous acid, it is converted into malic acid, whilst gen is disengaged:—

$$\overbrace{C_8H_8N_2O_6,\ 2\,HO}^{\text{Asparagin.}}+2\,NO_3=2\,\overbrace{HO,C_8H_4O_8}^{\text{Malic acid.}}+2\,N_2+2\,H_2O_2.$$

reaction is similar to that which occurs when the amides thus treated, and hence Piria was led to regard asparagin as tical with malamide; but on decomposing malic ether by ns of ammonia, a substance is obtained which is isomeric with ragin, but not identical with it. Asparagin forms combinations several of the acids in definite proportions; thus, the nitrate, alate, the dextrotartrate, and the hydrochlorate of asparagin be obtained in crystals without difficulty. The lævotartrate paragin forms an uncrystallizable syrup. It also combines bases, and even displaces acetic acid from acetate of lead.

144) *Aspartic Acid* ($HO,C_8H_6NO_7$).—If aspartate of am-a be boiled with baryta till the ammonia is entirely expelled, ate of baryta is formed; and from this salt the baryta may ecipitated by the cautious addition of sulphuric acid: on ating the solution thus obtained, aspartic acid crystallizes in rectangular *tables which have a silky lustre.* It is soluble

both in acids and alkalies; when dissolved in the alkalies it produces left-handed rotation of the plane of polarization, but if dissolved in acids the rotation is to the right.

Pasteur has discovered the existence of a second modification of aspartic acid which is without action upon polarized light. This *inactive* acid is obtained by heating bimalate of ammonia to about 360°, and boiling the residue (fumarimide, $C_8H_3NO_4$) for some hours with hydrochloric acid. The solution, when evaporated, yields crystals of hydrochlorate of aspartic acid ($HO,C_8H_6NO_7$, HCl). These crystals must be dissolved in water, and the solution divided into two equal portions; one of these is to be exactly neutralized by the addition of ammonia, and then added to the second portion; as the liquid cools, crystals of inactive aspartic acid are deposited in abundance. It is somewhat more soluble than the active variety, but in other respects resembles it in chemical properties.

Most of the aspartates are readily soluble in water. The acid appears in a few cases to form subsalts. Aspartic acid, when dissolved in nitric acid and saturated with nitrous acid, yields malic acid, whilst nitrogen is disengaged; and if the inactive variety be employed, the malic acid which is obtained is likewise of the inactive form (1142):—

$$\overbrace{2\,(HO,C_8H_6NO_7)}^{\text{Aspartic acid.}}+2\,NO_3=\overbrace{2\,(2\,HO,C_8H_4O_8)}^{\text{Malic acid.}}+2\,N_2+H_2O_2.$$

2. *Tartaric Acid, and its Derivatives.*

(1145) *Isomeric forms of Tartaric Acid.*—The remarkable researches of Pasteur (*Ann. de Chimie*, III. xxiv. 442, and xxviii. 56) upon the optical and chemical properties of tartaric acid, have opened a new and important method of investigating the molecular composition of organic bodies. He has proved the existence of two varieties of tartaric acid, which may be distinguished by the peculiarities of their crystals. The crystals of each variety of tartaric acid are always unsymmetrical; but the deficit in symmetry displayed by the crystals of one variety is exactly the reverse of that manifested by those of the other variety. Each of these forms of tartaric acid exerts a powerful effect of rotation upon a ray of polarized light; but the effect produced by equal quantities of the two varieties of the acid, though equal in amount, is opposite in direction. One of the modifications exhibits a crystalline form, which is termed *dextro-hemihedral*; its solution produces right-handed rotation o a ray of polarized light: this variety is known as *dextro-tartaric* *troracemic acid:* it is the usual form of the acid. The modification is *lævohemihedral,* and produces a left-handed n of a polarized ray: this modification constitutes *lævotar*-r *lævoracemic acid.* The two acids are so related in crys- form, that if a salt of the acid which is dextrohemi- be held before a mirror, the reflection of the crystal xactly represent the form of the corresponding crystal of the emihedral acid. Both these modifications are exactly r in chemical properties, so long as they are combined with s which exert no action upon polarized light; but this iden- n chemical properties disappears when they are united with s endowed with rotatory power upon polarized light: for ple, dextrotartaric acid forms with asparagin a crystalline ound, whilst the lævotartaric acid forms with this body a my mass.

When concentrated solutions of equal parts of dextrotartaric of lævotartaric acids are mixed together, the temperature considerably: and on cooling, crystals of a different acid formed. This new acid is identical with the *paratartaric acemic acid:* it has no longer the power of causing the ion of a ray of polarized light, and it presents differences chemical reactions (1149) from those of both of its com-nts.

Yet, if the acid thus obtained be divided into two equal parts, alf being neutralized with soda, then mixed with the other of the acid and neutralized with ammonia, the solution on ration will yield crystals, each of which has a powerful rota-action on polarized light; but the crystalline mass will be to consist of a mixture of the right-handed and of the nded double tartrate of soda and ammonia, in equal propor- The crystals of the two salts are recognised by their oppo-emihedral form, and may be separated by hand. If all the handed crystals be dissolved separately in water, and decom- by adding a solution of nitrate of lead, a precipitate con- of the dextrotartrate of lead will be deposited. From recipitate the dextrotartaric acid may be separated by means phuric acid, and may be obtained in crystals on evaporation: lævohemihedral crystals be treated in a similar manner, ric acid may also be procured.

was by treating the natural racemate of soda and ammonia manner, and picking out each crystal separately, that s enabled to prove *the existence of the* two modifica-*taric acid, and to show that* racemic acid consists of a mixture of two acids which exert opposite effects of rotation on polarized light.

Very few of the salts of racemic acid thus spontaneously separate into two different hemihedral varieties of crystalline form; the racemate of cinchonicine (1204) is easily separable into its component crystals, and the racemate of quinicine also exhibits a similar property. These salts may therefore be employed for the purpose of isolating the two modifications of tartaric acid, when they occur in combination: at a certain stage of concentration of the racemate of cinchonicine, the first crop of crystals consists chiefly of the lævotartrate. When racemate of quinicine is employed, the crystals which are first deposited consist mainly of the dextrotartrate.

(1146) ORDINARY TARTARIC ACID, or *Dextroracemic Acid* ($2\,HO,C_8H_4O_{10} = 18 + 132$).—The principal supply of this acid is obtained from the grape; but it is also present in the tamarind, and in the unripe berries of the mountain ash: it is likewise frequently met with in small quantity in other plants. Liebig also found it in the acid mother-liquor obtained in preparing mucic acid from sugar of milk. Grape juice contains it in the form of bitartrate, or, as it is sometimes called, supertartrate of potash, constituting the crust or tartar which is deposited in the vessel in which the wine is kept.

Preparation.—In order to prepare the acid, crude tartar is dissolved in boiling water, and chalk is added so long as effervescence occurs, 4 parts of tartar requiring about 1 part of chalk; an insoluble tartrate of lime is thus precipitated, and neutral tartrate of potash remains dissolved. Tartaric acid being dibasic, the change which occurs may be thus represented:—Two atoms of bitartrate of potash react upon two equivalents of carbonate of lime, and form one atom of dibasic neutral tartrate of lime, and one of dibasic neutral tartrate of potash; thus:—

$$2\,(\overbrace{KO,HO,C_8H_4O_{10}}^{\text{Bitartrate of potash.}}) + \overbrace{2\,CaO,C_2O_4}^{\text{Carbonate of lime.}} = \overbrace{2\,CaO,C_8H_4O_{10}}^{\text{Tartrate of lime.}} + \overbrace{2\,KO,C_8H_4O_{10}}^{\text{Tartrate of potash.}}$$
$$+ H_2O_2 + C_2O_4.$$

The tartrate of potash in solution may be decomposed by the addition of an equivalent quantity of chloride of calcium, and the whole of the tartaric acid may thus be separated as tartrate of lime:—

$$\overbrace{2\,KO,C_8H_4O_{10}}^{\text{Tartrate of potash.}} + 2\,CaCl = \overbrace{2\,CaO,C_8H_4O_{10}}^{\text{Tartrate of lime.}} + 2\,KCl.$$

The product of the two operations is well washed, and digested with oil of vitriol diluted with 6 or 8 times its weight of water:

for every 5 parts of tartar 3 parts of concentrated sulphuric acid are required; the solution is allowed to digest at a gentle heat, sulphate of lime is formed, and tartaric acid set free. When cool, the liquid is filtered, evaporated in leaden vessels to the consistence of syrup, and allowed to crystallize; the formation of crystals is favoured by the presence of an excess of sulphuric acid.

Properties.—The acid thus obtained assumes the form of oblique rhombic prisms; when pure they are colourless, transparent, and permanent in the air. Tartaric acid is very soluble in water, in alcohol, and in wood spirit; it has a sharp agreeable acid taste. If heated with the caustic alkalies, water is expelled, and oxalate and acetate of the base are formed :—

$$\overbrace{2\,HO,C_8H_4O_{10}}^{\text{Tartaric acid.}}+3\,(KO,HO)=\overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}}+\overbrace{2\,KO,C_4O_6}^{\substack{\text{Oxalate}\\ \text{of potash.}}}+3\,H_2O_2.$$

Its aqueous solution becomes mouldy when long kept, and is slowly converted into acetic acid.

The crystals of tartaric acid, when gently heated, become as strongly electrical as those of tourmaline. Its solutions, particularly when hot, exert a powerful right-handed rotation upon a ray of polarized light. When tartaric is boiled with nitric acid, oxalic acid is formed, together with an acid homologous with the malic. Tartaric acid exhibits considerable tendency to combine with oxygen. If it be boiled with peroxide of lead it undergoes decomposition, water and carbonic acid being produced, whilst formiate of lead remains in the solution :—

$$2\,\overbrace{HO,C_8H_4O_{10}}^{\text{Tartaric acid.}}+6\,PbO_2=2\,\overbrace{(PbO,C_2HO_3)}^{\text{Formiate of lead.}}+2\,\overbrace{(2\,PbO,C_2O_4)}^{\text{Carbonate of lead.}}+2\,H_2O_2.$$

The salts of silver, of gold, and of platinum are also reduced when boiled with tartaric acid.

Tartaric acid is extensively used by the calico-printer and dyer for the removal of certain mordants from particular portions of the cloth. It is also used in the preparation of effervescing draughts with the bicarbonates of the alkalies.

An interesting relation exists between tartaric and succinic acids, in consequence of which tartaric may be reduced to succinic acid by saturating its concentrated aqueous solution with hydriodic acid, sealing it up in a strong glass tube and heating it, for 6 or 8 hours, to a temperature not exceeding 250° (Schmitt, *Liebig's Annal.*, cxiv. 109) :—

$$\overbrace{2\,HO,C_8H_4O_{10}}^{\text{Tartaric acid.}}+4\,HI=2\,\overbrace{HO,C_8H_4O_6}^{\text{Succinic acid.}}+2\,I_2+2\,H_2O_2;$$

and succinic acid may, in turn, be re-converted into tartaric acid by changing it first into bibromosuccinic acid, and then decomposing this compound with oxide of silver (Perkin and Duppa; 1132). Dessaignes, by treating tartaric acid with a mixture of phosphorus and iodine, also procured succinic acid, and at the same time obtained malic acid in the mother-liquor, the tartaric acid losing first 2 atoms of oxygen, thus furnishing malic acid, and this acid in turn losing 2 atoms more of oxygen, thus yielding the succinic.

(1147) *Tartrates.*—The tartaric is a dibasic acid,* and it consequently has a strong tendency to form double salts, three varieties of which may be distinguished:—

1. Salts which contain protoxides only; such as—

Rochelle salt	$KO,NaO,C_8H_4O_{10}+8\ Aq$,
Cream of tartar	$KO,HO,C_8H_4O_{10}$
Tartrate of copper and potash	$KO,CuO,C_8H_4O_{10}$.

2. Salts which contain both protoxides and sesquioxides, but in which the sesquioxide is combined with the same proportion of acid as the protoxide; such as—

Tartrate of potash and iron	$KO,Fe_2O_3,C_8H_4O_{10}$
Tartrate of potash and chromium	$KO,Cr_2O_3,C_8H_4O_{10}+7\ Aq$,
Tartrate of potash and uranium	$KO,U_2O_3,C_8H_4O_{10}+2\ Aq$.

3. Salts analogous to tartar emetic:—

Tartar emetic, or tartrate of potash and antimony	$KO,SbO_3,C_8H_4O_{10}+Aq$,
Tartrate of silver and antimony	$AgO,SbO_3,C_8H_4O_{10}$
Neutral tartrate of antimony	$2\ SbO_3,C_8H_4O_{10}+2\ Aq$,
Tartrate of potash and boracic acid	$KO,BO_3,C_8H_4O_{10}$
Tartrate of potash and arsenious acid	$KO,AsO_3,C_8H_4O_{10}+5\ Aq$.

The salts of this third class, with the exception of the compound with arsenious acid, are remarkable for the property which they possess, when apparently anhydrous, of losing two additional atoms of water, so as to present a composition which may be regarded as exhibiting a certain resemblance to that of tartaric

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[*] It is, however, probably formed on the tetratomic type, the atomicity and basicity being different, as in the case of the glycolic group, which would account for the anomalous effect of heat in expelling two atoms of water from certain of the anhydrous tartrates, as will be mentioned immediately; $2\ HO,C_8H_4O_{10}$ being probably in the type $\left.\begin{matrix}H_4\\H_4\end{matrix}\right\}O_8$, or $\left.\begin{matrix}C_8H_2O_4\\H_2H_2\end{matrix}\right\}O_8$, the normal tartrates, such as tartrate of potash, being $\left.\begin{matrix}C_8H_2O_4\\H_2K_2\end{matrix}\right\}O_8$.

anhydride (Gerhardt): SbO_3 (or its equivalent representative BO_2), being able to occupy the position of 1 atom of hydrogen in the compound; thus:—

At ordinary temperatures,

Tartaric acid	consists of	$C_8H_6O_{12}$,
Neutral tartrate of antimony	,,	$C_8H_4\ 2\,(SbO_2)O_{12}+2\,Aq$,
Tartar emetic	,,	$C_8H_4K\ (SbO_2)O_{12}+\ Aq$,
Tartrate of silver and antimony	,,	$C_8H_4Ag\ (SbO_2)O_{12}$
Tartrate of potash and boracic acid	,,	$C_8H_4K\ (BO_2)O_{12}$

But when heated they become, respectively,

Tartaric anhydride	$C_8H_4O_{10}$
Neutral tartrate of antimony at 374°	$C_8H_2\ 2\,(SbO_2)O_{10}$
Tartar emetic dried at 392°	$C_8H_2K\ (SbO_2)O_{10}$
Tartrate of silver and antimony at 320°	$C_8H_2Ag\ (SbO_2)O_{10}$
Tartrate of potash and boracic acid at 506°	$C_8H_2K\ (BO_2)O_{10}$.

Tartrate of Potash ($2\,KO,C_8H_4O_{10}=226$) crystallizes readily; it is somewhat deliquescent, and very soluble. The *bitartrate of potash* ($KO,HO,C_8H_4O_{10}=188$) is the ordinary source of the compounds of tartaric acid: it constitutes the crude tartar or *argol* of commerce, and is gradually deposited from all wines, forming a crust upon the inside of casks in which the wine is stored. This salt is very sparingly soluble in cold water, of which it requires about 180 parts for solution; boiling water dissolves about one-sixth of its weight of it, and deposits the salt in oblique rhombic prisms, which when pure are of snowy whiteness, forming common *cream of tartar*. It produces a gritty sensation under the teeth, and has a sour taste. When heated to redness in covered vessels the acid is decomposed, and a charred mass remains, consisting of carbonate of potash and unconsumed carbon; this product is often used in the laboratory under the name of *black flux*. If the salt be calcined with twice its weight of nitre, *white flux* is obtained; in this operation the carbon of the organic acid is completely burned, and carbonate of potash is left.

Tartrate of Potash and Soda, ($KO,NaO,C_8H_4O_{10}+8\,Aq=210+72$).—The atom of basic water may be displaced from cream of tartar by soda, and then a double salt, often called *Rochelle salt*, is produced: it forms large beautiful crystals which have the appearance of six-sided prisms, one half of which only is developed. The tartrates of *lime* ($2\,CaO,C_8H_4O_{10}+8\,Aq$), *baryta*, and *magnesia* are sparingly soluble. *Iron* forms with potash and ammonia double tartrates which are used in medicine: the potash salt when dried at 212° is anhydrous: the ammoniacal salt has the formula ($H_4NO,Fe_2O_3,C_8H_4O_{10}+4$ or $5\,Aq$).

Borotartrate of Potash; Soluble Tartar ($KO,BO_3,C_8H_4O_{10}$; at 212°).—When 1 part of boracic acid, 2 parts of cream of tartar, and

24 of water are heated together, a solution is formed, which on evaporation to dryness and treatment with alcohol (in order to remove the excess of boracic acid) furnishes the foregoing compound, in the form of a white non-crystalline powder, which is insoluble in alcohol, but very soluble in water; it becomes anhydrous at 212°, and if heated to 560° it loses 2 more equivalents of water, like tartar emetic under similar circumstances. This salt has been employed medicinally as a purgative.

Tartrates of Antimony.—Several tartrates of antimony may be formed. These salts are remarkable for the property which they possess, when apparently anhydrous, of losing 2 equivalents of water, so as to present a composition corresponding to that of tartaric anhydride. The most important of these compounds is known as *tartarized antimony* or *tartar emetic* ($KO,SbO_3,C_8H_4O_{10} + Aq = 325 + 9$), which has long been extensively used in medicine. Tartar emetic may be prepared in various ways; one of the best is the following:—3 parts of oxide of antimony (obtained by boiling to dryness sulphuric acid upon metallic antimony and washing the residue with carbonate of soda) are mingled with 4 parts of cream of tartar, and made into thin paste with water. This mixture is allowed to digest for some hours, and is then boiled with 6 or 8 parts of water. The solution thus formed is filtered while hot, and allowed to crystallize: as the liquid cools the salt is deposited in the form of square prisms, the primary form of which is an octohedron, with a rhombic base. Tartar emetic is soluble in about 15 parts of cold water; its solution reddens litmus slightly. This salt is somewhat efflorescent; when dried at 212° it becomes anhydrous, and when heated to 400° it loses 2 additional equivalents of water, and then has a composition of $KO,SbO_3,C_8H_2O_8$; if this body be redissolved in water, it furnishes ordinary tartar emetic. A solution of tartarized antimony acts as a violent emetic and carthartic poison. Sulphuretted hydrogen throws down the orange-coloured sulphide of antimony from it, and the alkalies and their carbonates occasion a precipitate of oxide of antimony.

The place of the potash in ordinary tartar emetic may be supplied by soda, ammonia, oxide of silver, and oxide of lead; the lead and silver salts thus formed lose 2 equivalents of water at a high temperature in the same manner as the potash salt.

A compound similar to tartar emetic may be formed with arsenious acid ($KO,AsO_3,C_8H_4O_{10}$).

The mother-liquors from which tartar emetic has been prepared, often deposit a compound which may be crystallized with difficulty in oblique rhombic prisms [$KO,SbO_3,2\,HO,2\,C_8H_4O_{10}$

q; Knapp]: it is a combination of tartar emetic with an
ual atom of tartaric acid. Knapp has also obtained a com-
of tartar emetic with cream of tartar [$KO,SbO_3,C_8H_4O_{10}$
$KO,HO,C_8H_4O_{10}$)], by boiling 5 parts of tartar emetic with 8
am of tartar, and a small quantity of water; it is deposited
ringly soluble pearly scales. If oxide of antimony be dis-
in tartaric acid, the addition of alcohol in excess occasions
paration of a granular white precipitate, which, according
erzelius, has a composition represented by the formula
$O_3,C_8H_4O_{10}+2$ Aq. According to Péligot an acid tartrate
[$O,SbO_3,2\,C_8H_4O_{10}+5$ Aq] may be obtained in large crystals
solution of oxide of antimony in excess of tartaric acid.

The presence of tartaric acid in solution is detected, if the
be moderately concentrated, by the addition of acetate
potash; a few drops of free acetate acid must also be
if the solution be neutral; under these circumstances
ringly soluble bitartrate of potash falls, the quantity of
is much increased by briskly stirring the mixture. With
of silver a sparingly soluble tartrate of silver is formed:
precipitate when placed on platinum foil becomes charred,
up on the application of heat, and leaves a residue of pure
. A solution of sulphate of lime is not precipitated by a
on of tartaric acid. Lime-water in excess occasions a pre-
te, which disappears on the addition of sal-ammoniac.
ide of calcium and acetate of lead give white precipitates in
al solutions of the tartrates.

The presence of tartaric acid in a solution which contains salts
or of copper prevents the precipitation of the oxides of these
on the addition of an alkali. This property is sometimes
advantage of in the operations of analysis.

The tartrates when heated strongly become blackened and are
posed, emitting an odour of burnt sugar.

148) *Action of Heat on Tartaric Acid.*—The action of heat
tartaric acid is remarkable. If heated to about 340° it
and without losing weight is changed into two metameric
etatartaric and *isotartaric* acids. Metatartaric acid forms
escent uncrystallizable mass: it is dibasic, but its salts
re soluble than the ordinary tartrates, into which they are
ed by boiling their solutions.

rtaric acid ($HO,C_8H_5O_{11}$) assumes the form of a vitreous
t mass. It is a monobasic acid, and forms salts which are
th the bitartrates, but are much *more* soluble; by boiling
ns they *become converted into* ordinary bitartrates.

If tartaric acid be heated to 374°, it fuses; two atoms of the acid lose one equivalent of water, and thus become converted into a new acid, termed by Fremy the *tartralic*. In order to isolate this compound, the mass is dissolved in water and neutralized with carbonate of baryta; a soluble tartralate of this base is formed, while any undecomposed tartaric acid remains behind in the form of an insoluble tartrate of baryta. Aqueous solutions of tartralic acid and of its salts, if boiled, pass quickly into the ordinary tartrates, and the same change takes place more slowly at ordinary temperatures. If tartaric acid be kept longer in fusion half its basic water is expelled, and *tartrelic acid* is formed, which gives a syrupy precipitate with salts of baryta. The two acids last described are probably mere combinations of the anhydrous with the crystallized tartaric acid, in different proportions.

If the temperature of the fused tartaric acid be cautiously maintained for some time at 374°, all its basic water is driven off, and *tartaric anhydride* remains in the form of a white porous mass; in order to remove any unchanged tartaric acid, it may be washed first with cold water, and then with alcohol, after which it should be dried *in vacuo*. It is insoluble in water, alcohol, and ether, but if allowed to remain long moist it gradually becomes soluble, and is converted into crystallized tartaric acid. The last three compounds present a relation somewhat analogous to those of the varieties of phosphoric acid; for instance, if they be compared with 2 atoms of tartaric acid, the relations will be thus represented:—

Tartaric anhydride	$C_{16}H_8O_{20}$
Tartrelic acid	$2\,HO,C_{16}H_8O_{20}$
Tartralic acid	$3\,HO,C_{16}H_8O_{20}$
Crystallized tartaric acid . .	$4\,HO,C_{16}H_8O_{20}$

By heating crystallized tartaric acid to about 400° in a retort, an acid liquor distils, which contains acetic acid, and a new acid termed *pyruvic* or *pyroracemic* acid ($2\,HO,C_{12}H_6O_{10}$). It forms an insoluble salt with lead, and a sparingly soluble one with silver. Pyruvic acid is characterized by the production of a red solution when mixed with a solution of a protosalt of iron. If its salts be prepared in the cold, they are crystallizable; but if the acid be saturated with bases at a high temperature, the salts are gummy and do not crystallize.

During the distillation of tartaric acid, a quantity of a second new acid is also formed; it crystallizes in oblique rhombic prisms, and has received the name of *pyrotartaric acid* ($2\,HO,C_{10}H_6O_6$);

it contains the elements of two equivalents of carbonic acid less than the pyruvic. Pyrotartaric acid is dibasic, it forms both normal and acid salts; the latter crystallize with facility.

(1149) *Racemic*, or *Paratartaric Acid* ($2\ HO,C_8H_4O_{10}+2\ Aq$).—Some varieties of the grape, particularly those grown in the Vosges district, present a singular modification of tartaric acid, which is metameric with the tartaric acid, and equal amounts of the two acids saturate equal quantities of the same base. This acid, as has been already stated (1145), is plainly a compound of dextrotartaric and lævotartaric acids: it is without action upon polarized light.

Racemic acid generally accompanies tartaric acid in greater or less quantity. It is obtained from the racemate of lime by a process precisely similar to that used for procuring tartaric acid from the tartrate of lime. Racemic acid crystallizes more readily than the tartaric, in efflorescent, oblique rhombic prisms, which contain two equivalents of water of crystallization; this water is expelled by a temperature of 212°. Racemic acid is less soluble in alcohol than tartaric acid; it slowly precipitates solutions of sulphate of lime as well as those of chloride of calcium; the racemate of lime is soluble in hydrochloric acid, and is precipitated unchanged on adding ammonia. These reactions distinguish it easily from tartaric acid. When heated, racemic acid loses water, and forms acids corresponding with the tartralic and tartrelic; it may ultimately be rendered anhydrous: the products of its distillation are the same as those of tartaric acid. With antimony it forms a salt which corresponds to tartar emetic, but it crystallizes in radiated tufts of needles, not in octohedra. The ordinary salts of racemic acid occur in symmetrical crystals; and, with the exception of the double racemate of soda and ammonia and of the racemate of cinchonicine and quinicine, they are not hemihedral. According to Pasteur (*Comptes Rendus*, xlvi. 615), if a solution of racemate of ammonia be mixed with about 1-2000th its weight of any albuminous substance, and be placed whilst hot in a flask with a long neck, which is filled with the liquid to the bottom of the neck, and if when it has cooled to about 80° a small quantity of a solution of a tartrate in active fermentation be added, fermentation will then be set up, and the liquid will acquire a power of rotation to the left. The lævotartaric acid will resist the fermentation, whilst the dextrotartaric acid disappears. If a solution of ordinary tartrate of ammonia be substituted for the racemate, the tartaric acid will disappear entirely.

(1150) *Conversion of Tartaric into Racemic Acid.*—Pasteur has succeeded in converting both the varieties of tartaric into racemic acid: for this purpose either the dextrotartrate or the lævotartrate of cinchonia is exposed to a gradually rising temperature; the salt first becomes converted into tartrate of cinchonicine: if the heat be continued, the cinchonicine loses water, it becomes coloured, and is transformed into quinoidine. At the same time the tartaric acid also becomes modified, and after it has been exposed to a temperature of 340° for five or six hours, a portion of it is changed into racemic acid. The black resinoid mass into which the salt has been converted, is treated with boiling water, and the liquid thus obtained is mixed with an excess of chloride of calcium, by which the whole of the racemic acid is precipitated in the form of racemate of lime, from which the acid may readily be extracted. During the process of converting the tartrate of cinchonia into the racemate, another modification of tartaric acid is formed; it has been termed by Pasteur, *inactive tartaric acid*, in allusion to its want of action upon polarized light. It crystallizes beautifully, and forms crystallizable salts. This inactive acid is distinguished from racemic acid, by the circumstance that it does not admit of being resolved into dextrotartaric and lævotartaric acids.

The following are the modifications of tartaric acid which are at present known:—

1. Tartaric anhydride (insoluble) . .	$C_8H_4O_{10}$
2. Dextrotartaric acid	$2\ HO,C_8H_4O_{10}$
3. Lævotartaric acid	$2\ HO,C_8H_4O_{10}$
4. Racemic acid	$2\ HO,C_8H_4O_{10}+2Aq,$
5. Inactive tartaric acid	$2\ HO,C_8H_4O_{10}$
6. Metatartaric acid	$2\ HO,C_8H_4O_{10}$
7. Isotartaric acid	$HO,C_8H_5O_{11}$
8. Tartralic acid	$1\frac{1}{2}\ HO,C_8H_4O_{10}$
9. Tartrelic acid	$HO,C_8H_4O_{10}$.

3. *Citric Acid, and its Derivatives.*

(1151) CITRIC ACID ($3\ HO,C_{12}H_5O_{11}+2\ Aq=27+165+18$; Liebig) is a powerful tribasic vegetable acid, found principally in the fruits of the *Aurantiaceæ*. Citric acid is also of frequent occurrence in other acidulous fruits, such as gooseberries, raspberries, strawberries, cherries, and tamarinds. It is extracted by neutralizing the juice of the lime or of the lemon with chalk, and decomposing the insoluble citrate of lime with sulphuric acid, by a process similar to that directed for the preparation of tartaric acid. Citric acid is very soluble in water; the solution has an agreeable acid taste: it is likewise soluble in alcohol, but not in ether. If the cold saturated aqueous solution be allowed to evaporate spontaneously, it crystallizes in colourless, transparent rhombic prisms, which constitute the commercial citric acid. When heated to 212° these crystals melt, and lose 2 Aq; the remaining compound consists of $C_{12}H_8O_{14}$, which Liebig regards as a tribasic hydrate of the acid ($3\ HO,C_{12}H_5O_{11}$). If a solution of the acid, instead of being allowed to evaporate spontaneously, be crystallized at 212°, crystals are formed which contain ($C_{12}H_9O_{15}$).* These crystals do not lose the additional atom of water until they are heated to 266°, when they become converted into the compound ($3\ HO, C_{12}H_5O_{11}$).

A diluted aqueous solution of citric acid gradually becomes mouldy, and undergoes decomposition, acetic acid being formed. Citric acid dissolves zinc and iron with evolution of hydrogen. When heated to about 100° F., with concentrated sulphuric acid, citric acid evolves pure carbonic oxide; but if the temperature be raised, acetone and carbonic acid are given off. Concentrated nitric acid converts citric acid into a mixture of acetic, oxalic, and carbonic acids. When heated with hydrate of potash, it is converted into oxalate and acetate of that base:—

$$\overbrace{3\ HO,C_{12}H_5O_{11}}^{\text{Citric acid.}}+4\,(KO,HO)=2\,\overbrace{(KO,C_4H_3O_3)}^{\text{Acetate of potash.}}+2\,\overbrace{KO,C_4O_6}^{\text{Oxalate of potash,}}+3\,H_2O_2.$$

Citric acid is extensively consumed by calico-printers for discharging the mordant from the cloth in patterns; it is likewise employed in dyeing silk with safflower, and for heightening the tint of cochineal: it is also used medicinally. Lemon juice is largely employed as an antiscorbutic.

(1152) *Citrates.*—Citric acid, being tribasic, forms three series of salts, which correspond to the varieties of the tribasic phosphates; for instance, 3 citrates of soda, having the following composition, may be obtained:—

1st. ($3\ NaO,C_{12}H_5O_{11}+11\ Aq$);
2nd. ($2\ NaO,\ HO,C_{12}H_5O_{11}+2\ Aq$);
and 3rd. ($NaO,2\ HO,C_{12}H_5O_{11}+2\ Aq$).

Citrate of lime ($3\ CaO,C_{12}H_5O_{11}+4\ Aq$) is the most important of the citrates, since it is largely employed in the preparation of

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* These Berzelius regarded as constituting true citric acid ($HO,C_4H_2O_4$, or rather $3\ HO,C_{12}H_6O_{12}$).

the acid ; it also serves as a test by which citric acid may be re-
cognised :—when the free acid is added to cold lime-water
quantity not sufficient to destroy its alkaline reaction, no pre
tate is produced ; but on boiling the solution, the citrate of lim
is deposited. This salt is soluble without effervescence, in dil
acetic, hydrochloric, or nitric acid. The addition of an exces
ammonia in the cold does not re-precipitate it from these so
tions ; but upon heating the ammoniacal liquid, the citrate
thrown down, and it is redissolved on cooling, if the quantity
not too considerable : these phenomena depend upon the circu
stance, that the citrate of lime is less soluble in boiling than
cold water. Crude citrate of lime, obtained by saturating lem
juice with chalk, cannot be preserved in a moist state with
undergoing decomposition : it ferments, disengages a mixture
hydrogen and carbonic acid gases, and a mixture of acetate and
butyrate of lime is formed :—

$$2\overbrace{(3CaO,C_{12}H_5O_{11})}^{\text{Citr. lime.}}+4\,H_2O_2=\overbrace{CaO,C_8H_7O_3}^{\text{Butyr. lime.}}+\overbrace{CaO,C_4H_3O_3}^{\text{Acet. lime.}}+2\overbrace{(2\,CaO,C}^{\text{Carb.}}$$

$$+4\,H_2+4\,C_2O_4.$$

This change is accelerated by the addition of a small quantity
yeast to the mixture.

The citrates of the alkalies are all soluble in water ; so al
are many of the citrates of the heavier metals ; the citrates of t
earths with 3 equivalents of the earthy base are insoluble ; b
become dissolved by adding an excess of citric acid, and th
form salts, which contain 1 equivalent or 2 equivalents of ba
water. The *acid citrate of lime* consists of 2 $CaO,HO,C_{12}H$
+ 2 Aq, and forms brilliant foliated crystals.

The citrates of the normal type, when heated, present a r
markable peculiarity, which led Berzelius to propose the formu
($HO,C_4H_2O_4$) or rather ($3\,HO,C_{12}H_6O_{12}$), as the true represen
tive of citric acid. Assuming, for example, that the formula
citrate of potash is ($3\,KO,C_{12}H_6O_{12}+Aq$), this salt, by a hea
212°, loses 2 HO, and is converted into ($3\,KO,C_{12}H_5O_{11}$), wh
is Liebig's formula for anhydrous citrate of potash. This resi
appears not to be a simple citrate of potash, though on redissolvi
it in water the original citrate is reproduced ; but it presents t
characters of a mixture of citrate and aconitate of potash ; if
the salt be treated with absolute alcohol, and decomposed by
hydrochloric acid, so as to exclude the access of water, chloride
potassium is formed, and the citric acid which is set free is fo
to be mixed with aconitic acid, which may be separated from

ic acid without difficulty. The same phenomenon is exhibited citrate of silver: if this salt be precipitated at a temperature w 50° F., it has a composition represented by the formula gO,$C_{12}H_6O_{12}$), but at all higher temperatures it contains an n less of water (3 $AgO, C_{12}H_5O_{11}$). Now, if this latter salt reated like the potash salt, with dry hydrochloric acid in lute alcohol, 3 atoms of the compound yield by decomposition oms of chloride of silver, 2 atoms of hydrated citric, and 1 n of hydrated aconitic acid:—

$$\overbrace{AgO,C_{12}H_5O_{11})}^{\text{Citrate of silver.}}+9\,HCl=\overbrace{(3\,HO,C_{12}H_3O_9)}^{\text{Aconitic acid.}}+2\,\overbrace{(3\,HO,C_{12}H_6O_{12})}^{\text{Citric acid.}}+9\,AgCl.$$

When citrate of silver is heated to 212° in a current of gen gas, it becomes partially reduced, and a brown powder med, which, according to Wöhler, is a citrate of suboxide of er. Water extracts citric acid from it, and dissolves it in ll proportion, producing a red solution. This solution, when ed, deposits reduced silver.

Citrate of peroxide of iron is prepared by dissolving hydrated xide of iron in a hot solution of citric acid. It has a sweetish e, and forms a deep brown liquid, from which it is precipitated the addition of alcohol. When its solution is evaporated in llow vessels, it forms brilliant scales of a resinous aspect; and this form it is used in medicine. The presence of citric acid vents the precipitation of peroxide of iron from its solution dding ammonia in excess.

Tribasic citrate of lead (dried at 250°; 3 $PbO,C_{12}H_5O_{11}$).—This is prepared by precipitating a hot alcoholic solution of tribasic te of soda by an alcoholic solution of acetate of lead; it forms nular sparingly soluble powder. If this salt be digested with onia, it forms a heavy crystalline powder (4 $PbO,C_{12}H_5O_{11}$ O); and if the tricitrate be digested with basic acetate of , a salt with a still larger proportion of base (6 $PbO,C_{12}H_5O_{11}$ O) is formed.

Tribasic citrate of copper is soluble: a green crystalline, spar- y soluble *subcitrate* (4 $CuO,C_{12}H_5O_{11}+5\,HO$) is formed by ng a solution of acetate of copper with citric acid.

tribasic citric ether (3 $C_4H_5O,C_{12}H_5O_{11}$) may be obtained by g an alcoholic solution of citric acid with hydrochloric tralizing with carbonate of soda, and agitating the liquid inary ether. The ethereal solution rises to the surface ing; and if the ethylic *ether be expelled* by the heat of a h, *citric ether is left as a colourless oily* liquid.

(1153) *Action of Heat upon Citric Acid.*—If citric acid exposed to a high temperature, it undergoes decomposition: temperature of between 300° and 350°, water, acetone, and a ture of carbonic acid and carbonic oxide gases are discngaged, a brownishe residu is obtained, which is in great part soluble ether. This residue consists of a peculiar acid, the *aconitic* (3 $C_{12}H_3O_9$), which exists also in the different varieties of mo hood (*Aconitum*) and marestail (*Equisetum*). Aconitic acid isomeric with fumaric and malæic acids. Hydrated aconitic contains the elements of 2 atoms of water less than hydrated acid; $3\ HO,C_{12}H_3O_9+H_2O_2=3\ HO,C_{12}H_5O_{11}$. Indeed, aco acid derives its principal interest from its close connexion citric acid, and from the light which its composition throws some apparent anomalies in relation to the separation of from the crystallized acid and its salts (1152). The aconitat the alkalies give no immediate precipitate in solutions of the of baryta, lime, magnesia, and zinc, but they produce white pitates in solutions of lead and of silver.

If citric acid be heated beyond the point at which aco acid is formed, the aconitic acid is itself decomposed, car acid escapes, and the principal product consists of a volatile, looking acid liquid, which contains a mixture of two isom acids, one of which, the *itaconic*, crystallizes with facility, and other, termed *citraconic*, *pyrocitric*, or *citribic acid*, is much soluble; both have the formula ($2\ HO,C_{10}H_4O_6$). 1 atom of drated aconitic acid contains the elements of 1 atom of hyd itaconic or citraconic acid, and 1 atom of carbonic acid:—

$$3\ \overbrace{HO,C_{12}H_3O_9}^{\text{Aconitic acid.}} = 2\ \overbrace{HO,C_{10}H_4O_6}^{\text{Itaconic acid.}} + C_2O_4.$$

A considerable quantity of citraconic anhydride passes over the hydrated acids during the distillation. Citraconic acid is obtained during the distillation of lactic acid. When citrac treated with nitric acid it is partially decomposed, and conv into oxalic acid, whilst a nitro-acid, probably ($2\ HO,C_{10}H_{13}NO$ is produced, and at the same time a new acid, isomeric with citraconic, is formed, termed *mesaconic acid.* The latter m obtained in minute crystals, which are sparingly soluble in

4. *Meconic Acid and its Derivatives.*

(1154) MECONIC ACID ($3\ HO,C_{14}HO_{11}+6\ Aq$).—This (which derives its name from μήκων, a poppy) is contained milky juice of the *Papaveraceæ*. It is extracted from a concentrated aqueous infusion of opium by nearly neutralizing it with milk of lime and adding a solution of chloride of calcium; the meconate of lime being nearly insoluble is thus precipitated. In order to isolate the acid, one part of meconate of lime is mixed with 10 parts of water at 190°, and decomposed by the addition of hydrochloric acid in considerable excess; the meconic acid crystallizes from the solution in scales, which, however, are considerably coloured. They must be digested with purified animal charcoal, and re-crystallized, but they cannot be obtained colourless without considerable difficulty. Meconic acid is sparingly soluble in cold water, but is readily dissolved by it when hot; it is also soluble in alcohol and in ether. Its solutions have an acid, astringent taste. When its crystals are heated to 212°, 6 atoms of water are expelled. The aqueous solution of meconic acid is decomposed by ebullition, and carbonic acid gradually escapes. This change is effected more rapidly if some mineral acid, such as the sulphuric or hydrochloric, be added to the liquid. Similar results are obtained if the crystallized acid be heated to 250°. In all these cases, a new acid, the comenic, is obtained.—

$$3\,\overbrace{HO,C_{14}HO_{11}}^{\text{Meconic acid.}} = 2\,\overbrace{HO,C_{12}H_2O_8}^{\text{Comenic acid,}} + C_2O_4.$$

Meconates.—Meconic acid is tribasic, the formula of its normal salts being $3\,MO,C_{14}HO_{11}$. The meconates of the alkalies are soluble. The normal meconates of lime, baryta, lead, copper, and silver are nearly insoluble in water, but are soluble in acetic acid. Meconate of silver when heated is decomposed with explosion.

It is sometimes important for medico-legal purposes to be able to ascertain the presence of meconic acid in cases where opium is suspected to have been administered as a poison. With this view the following process may be adopted:—The solution is to be mixed with acetate of lead, an impure meconate of lead is thus precipitated if meconic acid be present; the precipitate after it has been washed is decomposed by sulphuretted hydrogen, and the meconic acid thus set at liberty is concentrated by evaporation at a temperature not exceeding 160°; a very dilute solution of perchloride of iron is then added to the concentrated liquid. If meconic acid be present it strikes a deep blood-red colour, which may be distinguished from that due to sulphocyanide of potassium by the effect of the addition of a few drops of sulphuric acid with a fragment of zinc; if the colour be due to the sulphocyanide, the red tint will disappear, and sulphuretted hydrogen will be extricated; but if the compound contain meconic acid, the colour will not be affected: a solution of terchloride of gold or of corrosive sublimate also discharges the colour of the sulphocyanide of iron, but is without effect upon the meconate.

(1155) *Comenic acid* ($2\,HO,C_{12}H_2O_8$) is dibasic. It is sparingly soluble in water, and crystallizes in hard, warty nodules. Nitric acid rapidly decomposes it into oxalic, carbonic, and hydrocyanic acids. This acid, like the preceding one, gives a blood-red solution with the persalts of iron, and a white precipitate with acetate of lead, but it gives no precipitate with salts of baryta.

If either the meconic or the comenic acid be distilled, a new monobasic acid, *pyromeconic* acid ($HO,C_{10}H_3O_5$), is sublimed :—

$$2\,\overbrace{HO,C_{12}H_2O_8}^{\text{Comenic acid.}} = \overbrace{HO,C_{10}H_3O_5}^{\text{Pyromeconic acid.}} + C_2O_4.$$

This acid is isomeric with the pyromucic, but is distinguished from it by yielding with the persalts of iron a solution of a blood-red colour, and by giving no precipitate with a solution of subacetate of lead.

5. *Different Varieties of Tannic Acid.*

(1156) The term *tannin* was formerly applied to the various forms of the astringent principle which were employed in the process of tanning hides. Most of these substances are now known to possess an acid reaction; but it has been ascertained that there are several distinct compounds which resemble each other in properties, though they possess a different chemical composition. These astringent principles are very extensively diffused throughout the vegetable kingdom. The bark and leaves of most forest trees, such as the oak, the elm, the willow, the horse-chesnut, and the pine—and of many fruit trees, such as the pear and plum, contain tannin in notable quantity. The wood and bark of many shrubs, such as the sumach and the whortleberry—and the roots of the tormentilla and bistort, are also powerfully astringent, owing to the presence of one of the forms of tannin. Coffee and tea, as well as Paraguay tea, likewise contain a modification of this astringent principle. All these bodies, except coffee, precipitate the persalts of iron of a bluish-black colour, or if a free acid be present, the solution assumes a dark-green colour. Many vegetables contain an astringent principle which precipitates the salts of iron of a dark-green instead of a blue colour: catechu and kino offer good instances of this variety of tannin. Some few astringent plants yield an infusion which precipitates iron of a grey colour, among which are matricaria, rhatany (*Krameria triandra*), and the common nettle (*Urtica urens*). Tannic acid in all its forms rapidly absorbs oxygen when moist.

The most important of these acids, and the one which has been most accurately studied, is the tannic acid of the gall nut, or *gallotannic* acid: that of the oak or *quercitannic* acid is also a distinct species (Stenhouse), as well as that of the fustic (*Morus tinctoria*): *moritannic acid*, as the latter variety is termed, is a yellow crystalline solid, which, according to the experiments of Wagner, may be represented by the formula ($C_{36}H_{16}O_{20}$). *Quinotannic* acid, or the tannin of the cinchona, according to Hlasiwetz, is represented by the formula ($C_{28}H_{19}O_{17}$?); and there is no doubt that the *mimotannic* acid or tannin of the catechu is a distinct variety, although from its proneness to change, the true composition of this substance is uncertain. Kino, valonia (the acorn-cups of the *Quercus ægilops*), and divi-divi (the pod of the legume of *Cæsalpinia coriaria*), all contain powerfully astringent compounds which, according to Stenhouse, are distinct from gallotannic acid.

(1157) Gallotannic Acid; *tannic acid* ($C_{54}H_{22}O_{34}$; Strecker).—This acid is obtained in a state of purity from the gall nut, an excrescence produced upon the leaves of a species of oak (*Quercus infectoria*), by the puncture of a small hymenopterous insect. The gall nut contains as much as two-thirds of its weight of tannic acid, and about two per cent. of gallic acid (Guibourt). In order to extract the tannic acid, Pelouze directs the gall nuts to be reduced to powder, and digested with about an equal weight of washed ether; the decanted liquid separates on standing, into two portions, the denser of which is of a yellow colour, and consists of a concentrated aqueous solution of tannic acid; the other portion is of a greenish colour, and is composed of ether holding gallic acid and colouring matter in solution. The yellow solution, when evaporated to dryness, yields a porous, pale buff-coloured residue of amorphous gallotannic acid. According to Stenhouse the tannic acid of sumach is identical with that of the gall nut, but it is not readily obtained in a pure form. Gallotannic acid is freely soluble in water; it reddens litmus paper, and dissolves the carbonates with effervescence. It has a purely and intensely astringent taste: it is soluble in dilute alcohol, but sparingly so in ether. Its diluted aqueous solution slowly absorbs oxygen from the air, and is converted into gallic acid; this process is favoured by the presence of a particular ferment which is contained in the gall nut. A solution of tannic acid in water is coagulated by chloride of potassium, and by many other salts. Sulphuric, hydrochloric, phosphoric, and some other acids also diminish its solubility, and precipitate it from a concentrated aqueous solution. Nitric acid converts it into oxalic and saccharic acids. If boiled with dilute sulphuric, or with hydrochloric acid, it is converted into sugar and gallic acid (Strecker); the latter crystallizes on cooling, whilst the glucose remains in solution:—

$$\overbrace{C_{54}H_{22}O_{34}}^{\text{Gallotannic acid.}}+5\,H_2O_2=3\,\overbrace{(3\,HO,C_{14}H_3O_7)}^{\text{Gallic acid.}}+\overbrace{C_{12}H_{12}O_{12},\,2\,Aq.}^{\text{Glucose.}}$$

A boiling concentrated solution of potash also decomposes tannic acid and occasions the formation of gallic acid. If air be admitted to the mixture, the acid last named is in turn decomposed into a black ulmin-like substance.

Gallotannates.—The composition of these salts is but imperfectly known, and there is considerable uncertainty whether the acid should be regarded as dibasic or as tribasic. A solution of gallotannic acid occasions a violet-black precipitate in solutions of the persalts of iron. It also causes precipitates in the solutions of the salts of morphia, quinia, brucia, and many other vegetable bases; these precipitates consist of gallotannates of the bases, and are readily soluble in acetic acid. The gallotannates of lead and antimony are white and insoluble. Those of the alkalies are soluble; their solutions have an astringent taste, and do not precipitate gelatin until some acid is added to liberate the gallotannic acid from the base. If the solutions of these salts be exposed to the air, especially if the base be in excess, they rapidly become brown, and are decomposed with absorption of oxygen. None of the gallotannates can be obtained in crystals.

The basis of ordinary writing ink is gallotannate of iron. Various recipes are given for its preparation: the following furnishes a very good ink:—Digest three quarters of a pound of bruised nut galls in a gallon of cold water, then add six ounces of sulphate of iron with an equal weight of gum arabic, and four or five drops of kreasote to prevent the ink from becoming mouldy. Let this mixture digest at ordinary temperatures for two or three weeks with occasional agitation; then allow it to settle, and decant for use. Oxalic acid and chlorine water readily discharge the colour of writing-ink, and they may be employed to remove ink-stains from linen. An ink-spot when washed with an alkaline soap becomes yellow, forming what is familiarly known as an iron-mould. This yellow stain is due to the oxide of iron, which constitutes the basis of the ink, and which has attached itself to oth, whilst the alkali of the soap has removed the tannic

he most remarkable compound of tannic acid, however, is hich it forms with *gelatin*, which constitutes the basis of r. The principles of the manufacture of this important sub- will be considered (1458) after the properties of gelatin been described. When a solution of gelatin or isinglass is to an aqueous infusion of any vegetable containing tannic a copious gelatinous precipitate occurs, which is soluble in of gelatin if the liquid be boiled. An excess of tannic revents the resolution of the compound. If a piece of raw reed from hair, be immersed in a solution of tannic acid, the inous tissue gradually combines with the acid, and retains it e form of leather, the supernatant liquid being ultimately etely freed from all traces of tannin, if the piece of skin be icient size.

hen gallotannic acid is subjected to a temperature of about , it is decomposed, and yields pyrogallic and metagallic acids 9, 1160), whilst water and carbonic acid are expelled. The ation of pyrogallic acid appears to be characteristic of gallo- ic acid, since the other varieties of tannin do not yield this ound (Stenhouse).

(1158) *Mimotannic Acid.*—The different species of catechu and ino, although derived from trees belonging to several different ral families, appear to contain the same modification of the gent principle, which, as already stated, differs in some ntial particulars from the gallotannic acid. Formerly, kino catechu were seldom employed in this country except for licinal purposes; but of late years they have been extensively by the dyer and the tanner, and have thus acquired consider- mportance, both commercially and chemically.

he essential constituents of catechu are *mimotannic acid* and hin, which are mixed with a brown substance, resulting from xidation of both these bodies.

Mimotannic acid is sparingly soluble in dilute sulphuric acid, ugh freely soluble in water. If a concentrated aqueous in- of catechu be mixed with a small quantity of dilute sul- acid, a precipitate occurs, at first consisting chiefly of matter; this may be removed, and on then gradually ncentrated sulphuric acid so long as it occasions a pre- imotannic acid is thrown down: this precipitate may be n a filter, *washed with dilute sulphuric* acid, pressed *lds of blotting-paper, and dissolved* in water. The excess of sulphuric acid is then removed by digestion with carbonate of lead, and the filtered liquid, when evaporated *in vacuo*, furnishes mimotannic acid nearly pure.

This substance is distinguished from gallotannic acid, by yielding a greenish grey precipitate with the persalts of iron; and by not precipitating a solution of tartar emetic: when subjected to heat, it does not furnish pyrogallic acid. Its solution absorbs oxygen and becomes of a dark red colour, leaving, when evaporated, a substance no longer completely soluble in water. Under these circumstances, according to Delffs, a certain quantity of catechin is formed, and remains in a crystalline condition.

Catechin ($C_{20}H_9O_8,HO$; Zwenger) is contained in the portion of catechu which is not soluble in cold water; it is soluble in three or four parts of boiling water, or of boiling alcohol; and when pure is deposited in minute colourless crystals. The caustic alkalies immediately attack it, causing it to absorb oxygen, when it becomes first yellow, then red, and finally black. Catechin precipitates perchloride of iron of a dark green colour. It is soluble in the dilute acids: when treated with oil of vitriol it gives a purple solution: nitric acid converts it into oxalic acid. Catechin is fusible at 422°: at a higher temperature it is decomposed, and amongst other products yields a crystallizable substance termed *pyrocatechin*, or *oxyphenic acid* ($C_{12}H_6O_4$). Lautemann has obtained pyrocatechin artificially by decomposing moniodo-salicylic acid by means of an alkali (*Lieb. Annal.* cxviii. 372). *Moritannic acid* ($C_{36}H_{16}O_{20}$) (the tannin of the *Morus tinctoria*, the yellow dye called *fustic*) yields the same product when submitted to distillation.

It has been suggested that the different varieties of tannic acid may be homologous terms of the same series; but the facility with which they undergo change renders their investigation a matter of great difficulty; and the accuracy of the formulæ assigned to these different compounds, with the exception of that of gallotannic acid, must be regarded as very doubtful.

6. *Gallic Acid, and its Derivatives.*

(1159) GALLIC ACID ($C_{14}H_6O_{10}+2\ Aq=3\ HO,C_{14}H_3O_7+2\ Aq$ $=27+143+18$).—This acid exists ready formed in the gall nut, in sumach, in valonia, and in a large number of other astringent vegetables, although the quantity in each is but small. It may readily be obtained by allowing an infusion of gall nuts, or the powdered galls moistened freely with water, to stand in a warm place for some weeks, exposed to the air: it quickly becomes ldy, absorbs oxygen, and emits carbonic acid, owing to the rrence of a species of fermentation, during which abundance allic acid is deposited in the form of crystals. The acid must urified by digestion with animal charcoal and re-crystallization boiling water. Gallic acid is also deposited from infusion of nuts, if kept in vessels from which air is excluded; but in this no evolution of gas occurs: the exact stages of these processes rmentation have not been clearly made out. Gallic acid may be obtained by boiling tannic acid with dilute sulphuric or ochloric acid, in which case water is assimilated and glucose t at liberty (1157). Lautemann, by converting salicylic acid di-iodo-salicylic acid, and treating this compound with car- of potash, has succeeded in obtaining gallic acid.

he acid crystallizes either in the form of delicate silky needles, brilliant oblique rhomboidal prisms, which require about 100 of cold water for their solution, but only 3 parts of boiling : they are freely soluble in alcohol, but only sparingly so in . When dried at 212° they lose 9·5 per cent., or 2 equiva- , of water.

Gallates.—According to Strecker, gallic acid is tribasic, and it three classes of salts, the general formulæ of which, are 2 $HO,C_{14}H_3O_7$; 2 $MO,HO,C_{14}H_3O_7$; and 3 $MO,C_{14}H_3O_7$: these salts there are salts with an excess of acid, and with of base; thus an acid salt of potash, [2 (KO, 2 $HO,C_{14}H_3O_7$) $O,C_{14}H_3O_7+2\,Aq$] may be obtained by adding an alcoholic of potash to an alcoholic solution of gallic acid. The of the alkalies speedily absorb oxygen, and become brown their solutions are exposed to the air, especially if an excess be present. Nearly all the gallates of the heavy metallic are insoluble. If an excess of gallic acid be added to a salt d, the precipitate is at first white and amorphous, but it lly becomes crystalline if left in contact with the liquid. e most characteristic reaction of this acid, is the formation deep, bluish black solution, when added to a mixture of the lts and persalts of iron: if the solutions be free from acid, particularly if a solution of bicarbonate of lime be added, ction is one of extreme delicacy. The salts of gallic acid cause a precipitate in solutions of gelatin.

hen gallic acid is exposed to a temperature of from 410° to it is wholly volatilized, and is converted into pyrogallic and ic acids:—

$$3\,\overbrace{HO,C_{14}H_3O_7}^{\text{Gallic acid.}} = \overbrace{C_{12}H_6O_6}^{\text{Pyrogallic acid.}} + C_2O_4\,;$$

but if the temperature be allowed to reach 480°, the pyrogallic acid in its turn suffers decomposition; water is expelled, and a dark ulmin-like body is formed, termed *metagallic acid*, which is insoluble in water, but soluble in alkaline solutions:—

$$\overbrace{C_{12}H_6O_6}^{\text{Pyrogallic acid.}} = \overbrace{C_{12}H_4O_4}^{\text{Metagallic acid.}} + H_2O_2.$$

(1160) *Pyrogallic Acid* ($C_{12}H_6O_6$).—This substance possesses but very feeble acid properties. It may be obtained by the sublimation of gallic acid, or of any vegetable extract which contains gallotannic acid. The extract may be placed in a shallow iron pan, which is covered with a sheet of bibulous paper, over which a cone of writing-paper is fastened; on applying a regulated sand heat, the pyrogallic acid is converted into vapour; it passes through the bibulous paper, and rises into the chamber formed by the paper cone, where it is condensed, and is prevented from falling back into the pan beneath, by the interposed sheet of filtering-paper. This method of sublimation, contrived by Mohr, is applicable in many other cases of a similar kind. Liebig mixes well-dried gallic acid with twice its weight of coarsely powdered pumice-stone, and heats the mixture in a retort, through which a current of dry carbonic acid is maintained: 31 or 32 parts of pyrogallic acid are thus obtained for every 100 parts of gallic acid employed.

Sublimed pyrogallic acid forms voluminous brilliant plates, which are freely soluble in water, alcohol, and ether: the solution has a bitterish taste, and does not redden litmus paper. When the acid is heated to about 240° it melts; and when further heated, it emits a colourless, irritating vapour. The acid may be preserved unchanged whilst dry, but its solution quickly becomes brown, and absorbs oxygen; and if a free alkali be added, the absorption of oxygen is so rapid, as to afford a valuable method of removing free oxygen from gaseous mixtures (296 *note*).

The alkaline solutions of pyrogallic acid rapidly assume an ntense reddish brown colour: this brown solution, according to Stenhouse (*Liebig's Ann.* xlv. 6), contains acetate and carbonate of the base. When the acid is dropped into milk of lime it produces a beautiful purplish red colour, which soon becomes of a dingy brown: this reaction is very characteristic. Pyrogallic acid, on account of the facility with which it absorbs oxygen, decomposes most of the salts of silver, of gold, and of platinum; but it forms a definite compound with oxide of lead, and dissolves freshly precipitated alumina. If a solution of pyrogallic acid be added to a boiling solution of tartar emetic, sparingly soluble pearly crystals

$_{12}H_5O_5$) are deposited. With protosulphate of iron, free roxide of this metal, pyrogallic acid gives a deep indigo-lution, which becomes green by the action of air: with of iron it forms a bright red solution.

ogallic acid is now extensively employed in photographic ns, for the purpose of developing the latent image upon ntiferous collodion film after it has been exposed to the f light (884).

(1) *Ellagic Acid* ($HO,C_{14}H_2O_7 + 2$ Aq.; if dried at 240°, H_2O_7).—During the preparation of gallic acid from gall quantity of a grey crystalline powder, termed *ellagic acid,* d: this substance is insoluble in water, but soluble in the : with potash it forms a flaky salt which is but sparingly the solution of this salt speedily absorbs oxygen from the becomes of a blood-red colour. When treated with a of perchloride of iron, ellagic acid is gradually dissolved, ns a deep blue liquid. The most singular circumstance in on with this body is the discovery of Wöhler and Merklein is a constituent of certain kinds of oriental bezoars. These are intestinal concretions which occur in the wild goats, es, and deer of the countries of Central Asia: they are ovoid, or reniform masses of a dark olive-green colour, d upon the surface, and in size seldom exceeding a pigeon's hen broken, they are usually found to have been deposited entric layers upon some foreign nucleus: they are not like the lithofellic bezoars.

centrated sulphuric acid dissolves ellagic acid, and precipi- unaltered, on dilution.

gallic or *Parellagic Acid* ($C_{14}H_4O_8 + 2$ Aq).—If the crystals c acid be dissolved in five times their weight of oil of a crimson solution is formed, which, if allowed to fall drop into water, deposits a reddish brown substance, partly in and partly in crystals. The crystalline portion, or *r acid,* is insoluble in water, but soluble in solutions of lies. This acid, when heated, yields a sublimate consisting red prisms, resembling those of alizarin. If a piece of hich has been moistened with alum, or with a salt of iron, d with rufigallic acid, it becomes dyed with the same tints dder had been used; but the colours are less brilliant than madder.

7. *Quinic Acid, and its Derivatives.*

2) *Quinic or Kinic Acid* (2 $HO,C_{28}H_{20}O_{20}$; Gerhardt).—

The bark of the cinchonas contains a peculiar modification of tannic acid, termed the quinotannic, and besides this, it furnishes the remarkable acid to which the name of *quinic* acid has been given. Quinic acid appears to exist in the bark in combination with lime and with the organic bases of the bark. If an aqueous decoction of cinchona bark be mixed with milk of lime until it assumes a feeble alkaline reaction, the vegetable bases and the tannic acid are precipitated, and quinate of lime remains in the liquid; this salt may be crystallized from the mother-liquor by evaporation, and decomposed by means of oxalic or of sulphuric acid. The quinic acid may then be obtained in crystals from the solution.

Quinic acid crystallizes in colourless, oblique rhombic prisms, which have a strongly acid taste; they are freely soluble in boiling water, less so in cold water, still less so in alcohol, and very sparingly soluble in ether. When heated to 311° the acid fuses, and at a higher temperature yields a complicated mixture containing amongst other matters, benzol, benzoic acid, carbonic acid, salicylous acid, and a colourless substance termed hydroquinone.

Quinates.—Quinic acid appears to be dibasic; nearly all its salts are soluble in water, with the exception of the subquinate of lead ($4\ PbO,C_{28}Pb_4H_{16}O_{20}$), which is obtained by adding a solution of subacetate of lead to a neutral quinate. It is remarkable that in this salt a portion of the hydrogen of the acid appears to have been displaced by lead. Quinic acid also forms a basic salt with copper ($4\ CuO,C_{28}H_{20}O_{20}+8\ Aq$), which may be obtained in brilliant green, sparingly soluble crystals.

(1163) *Quinone* or *kinone* ($C_{12}H_4O_4$).—When one part of quinic acid is heated with four parts of finely powdered peroxide of manganese and one part of sulphuric acid diluted with an equal weight of water, a beautiful yellow crystalline compound is sublimed, and condensed in the neck of the retort in long needles; to this substance the name of *quinone* has been given:—

$$\overbrace{2\ HO,C_{28}H_{20}O_{20}}^{\text{Quinic acid.}}+2\ O_4=\overbrace{2\ C_{12}H_4O_4}^{\text{Quinone.}}+2\ C_2O_4+7\ H_2O_2.$$

It may also be obtained from the aqueous extract of coffee by treating it in a similar manner. Quinone fuses at 212°. It is sparingly soluble in water, but is dissolved more freely by alcohol and by ether.

Hydroquinone ($C_{12}H_6O_4$).—When quinone is treated with reducing agents, such as sulphurous acid or protochloride of tin, first converted into a green compound, but it ultimately ishes a colourless body, termed *hydroquinone*. This sub-ce, mixed with benzoic acid, is the principal product of the distillation of quinic acid :—

$$2\,\overbrace{HO,C_{28}H_{20}O_{20}}^{\text{Quinic acid.}}=\overbrace{C_{12}H_6O_4}^{\text{Hydroquinone.}}+\overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}}+C_2O_4+5\,H_2O_2.$$

the simplest plan of preparing it consists in suspending quinone ater and transmitting sulphurous acid gas until the quinone is olved; by evaporating this solution, crystals of hydroquinone obtained, whilst the liquid contains sulphuric acid. Hydro-one forms six-sided, colourless prisms, which are very soluble ater, alcohol, and ether. It is without odour, and has a tish taste; it fuses readily, and may be sublimed in brilliant es, resembling those of benzoic acid.

The action of oxidizing agents upon hydroquinone is remark-. When its solution is mixed with a solution of sesquichloride on, the liquid immediately assumes a deep blackish-red colour, in a few moments it becomes filled with magnificent green ular crystals, which have a metallic lustre. These crystals ist of a combination of quinone with hydroquinone, which has n called *green hydroquinone*, ($C_{12}H_4O_4,C_{12}H_6O_4$). Chlorine, ic acid, nitrate of silver, and chromate of potash, when mixed h a solution of hydroquinone, also occasion the formation of the e compound: the same substance is likewise formed by mixing ution of quinone with one of hydroquinone. This beautiful pound fuses on the application of a gentle heat; it is partially mposed by a further elevation of temperature, and emits pours of quinone. It is freely soluble in boiling water, and ingly so in cold water; the solution has a styptic taste. ohol and ether dissolve it readily, and form yellow solutions.

Both quinone and hydroquinone yield several substitution pounds with chlorine, and with sulphur.

Perchloroquinone, or *chloranile* ($C_{12}Cl_4O_4$).—Of the chlorinated ivatives of quinone, the substance which has been designated *oranile* is the most interesting, since through this body the tion of quinone to the phenic, salicylic, and indigo groups of pounds is indicated. Perchloroquinone may be produced by action of a mixture of chlorate of potash and hydrochloric d upon quinone, and upon a variety of other substances; viz., aniline, on carbolic and carbazotic acid of the phenyl series, on icin, hydride of salicyl, and salicylic acid of the salicyl group, on isatin, and its *chlorinated derivatives* in the indigo group. *asiest method of obtaining it consists* in preparing a warm dilute solution of salicin acidulated with hydrochloric acid, and adding powdered chlorate of potash in small quantities at a time. A brisk reaction occurs on each addition of the chlorate, and a heavy orange-coloured oil is formed, which solidifies on cooling. This solid mass is perchloroquinone; it may be purified by crystallization from boiling alcohol. Perchloroquinone forms pale yellow flakes of pearly and metallic lustre. It may be sublimed unaltered by the application of a gentle heat. It is insoluble in cold water, and is but sparingly soluble in cold alcohol. Ether dissolves it rather more freely. A warm dilute solution of potash dissolves perchloroquinone readily, giving a purple liquid, which on cooling deposits scales of *bichloroquinonate* of potash ($2\ KO,C_{12}Cl_2O_6 + 2\ Aq$).

8 and 9. *Sorbic and Parasorbic Acids.*

(1163 *a*) Hofmann has recently pointed out the existence of an acid derived from the berries of the service-tree (*Q. J. Chem. Soc.* xii. 43), which he has termed sorbic acid ($HO, C_{12}H_7O_3$), and which is one of a group intermediate between the fatty and the aromatic acids. If we compare together the terms of the fatty and aromatic series which contain an equal number of atoms of hydrogen, the new acid will contain a number of atoms of carbon intermediate between them—*e.g.*, the three corresponding acids in each group are :—

$$\overbrace{HO,C_8H_7O_3}^{\text{Butyric acid.}} \quad ; \quad \overbrace{HO,C_{12}H_7O_3}^{\text{Sorbic acid.}} \quad ; \quad \overbrace{HO,C_{16}H_7O_3}^{\text{Toluic acid.}}.$$

The general formula of the group of fatty acids being $HO, C_{2n}H_{2n-1}O_3$, that of the sorbic group is $HO,C_{2n}H_{2n-5}O_3$, that of the benzoic group is $HO,C_{2n}H_{2n-9}O_3$. We may confidently anticipate the discovery of aldehyds, alcohols, and other acids of this family from the labours of future inquirers.

Parasorbic Acid ($HO,C_{12}H_7O_3$) : *Sp. gr. of liquid* 1·0681; *Boiling pt.* 430°.—If the juice of the unripe berries of the mountain-ash be partially neutralized with lime and submitted to distillation, an acid liquid passes over : after saturating this with carbonate of soda, concentrating the solution by evaporation and decomposing it by the addition of sulphuric acid somewhat diluted, a brownish oil rises to the surface of the liquid : it may be purified by solution in ether, and redistillation after the ether has been allowed to evaporate.

This oil has a peculiar, powerful, somewhat pungent aromatic odour; when pure it is colourless, is somewhat soluble in water, and abundantly so in alcohol and ether. It possesses the properties of an acid, which Hofmann calls *parasorbic;* it is readily soluble in solutions of the alkalies and alkaline earths.

On gently treating this oil with solid hydrate of potash, a transformation of the acid occurs analogous to that of oleic acid by the agency of peroxide of nitrogen. A new isomeric acid is formed termed sorbic acid. When the potash salt is decomposed by hydrochloric acid this compound is set at liberty, furnishing an oil which rapidly solidifies into a hard crystalline substance. A similar transformation of parasorbic acid occurs when the oil is boiled for a short time with concentrated hydrochloric acid. Oil of vitriol dissolves parasorbic acid, and on dilution the substance which is separated gradually becomes crystallized as sorbic acid.

Sorbic Acid ($HO,C_{12}H_7O_3$, *fusing pt.* 274°) as thus obtained is nearly insoluble in cold water, but moderately soluble in boiling water. Ether and alcohol both dissolve it very readily. It may be obtained crystallized in magnificent white needles by deposition from a hot solution in a mixture of 1 volume of alcohol and 2 volumes of water. On the application of heat it fuses, and at a higher temperature may be distilled unaltered.

The sorbates of potash and soda are very soluble, and crystallize with difficulty. Sorbate of ammonia is also very soluble, but crystallizes in slender needles. The salts of lime and baryta are less soluble, and crystallize in anhydrous silvery scales on adding alcohol to their boiling aqueous solutions.

CHAPTER VI.

AMIDES, AND ORGANIC BASES.

§ I. AMIDES AND THEIR VARIETIES.

(1164) *Amides.*—It has been already stated (312), that under certain circumstances a portion of the hydrogen of ammonia may be displaced by potassium, and a compound is thus formed consisting of KH_2N, which has been termed *amide* of potassium. When oxalate of ammonia is submitted to distillation, a white sublimate is obtained (507 *note*), in which the elements of oxalate of ammonia, minus 4 atoms of water, are present; to this sublimate Dumas, by whom it was discovered, gave the name of *oxamide*. The following equation represents the relation which exists between oxamide and oxalate of ammonia:—

$$2\ H_4NO,C_4O_6=2\ H_2N,C_4O_4+2\ H_2O_2.$$

Now it is found that other salts of ammonia, when submitted to dry distillation, or otherwise deprived of water, yield compounds analogous to oxamide. When the ammonia salts of the monobasic acids lose 2 atoms of water, or when the neutral ammonia salts of the dibasic acids lose 4 atoms of water, the resulting compounds are called *amides*; those obtained from the dibasic acids being further distinguished as *diamides*. It has been proposed to account for the formation of these compounds by the hypothesis, that they contain a certain hydride of nitrogen, which has not hitherto been procured in a separate form, but to which the composition H_2N, and the name of *amidogen* (312) has been assigned.

(1165) *Nitriles.*—But the amides themselves also admit of being deprived of water: and when the amide of a monobasic acid has thus been made to lose two additional atoms of water, it yields a compound belonging to a class known under the generic term of *nitriles*. Acetamide, less two atoms of water, yields aceto-nitrile:—

$$\overbrace{H_2N,C_4H_3O_2}^{\text{Acetamide.}} = H_2O_2+\overbrace{HN,C_4H_2}^{\text{Aceto-nitrile.}};$$

and, in like manner, oxamide gives oxalo-nitrile:—

$$2\ \overbrace{(H_2N)C_4O_4}^{\text{Oxamide.}} = 2\ H_2O_2+\overbrace{2\ NC_2}^{\text{Oxalo-nitrile.}}.$$

It is worthy of remark, that oxalonitrile has the same composition as cyanogen, and is not only metameric, but also identical with it; so that cyanogen admits of being regarded as the nitrile of oxalic acid; and thus a certain analogy may be traced between cyanogen and the products obtained by the dehydration of the ammonia salts; the nitriles of the fatty acids $HO,C_{2n}H_{2n-1},O_3$, being in fact identical with the hydrocyanic ethers (1000). These nitriles, when fused with potassium, yield cyanide of potassium and disengage hydrogen, mixed with gaseous hydrocarbons. The nitriles, when treated with an alkali, do not reproduce hydrocyanic acid, and their corresponding alcohol; but they recombine with the elements of water, and form ammonia, and a salt of the original acid from which the nitrile was obtained. Thus, benzonitrile when boiled with a solution of potash, yields benzoate of potash and ammonia :—

$$\overbrace{C_{14}H_5N}^{\text{Benzonitrile.}}+KO,HO+H_2O_2=\overbrace{KO,C_{14}H_5O_3}^{\text{Benzoate of potash.}}+H_3N.$$

The nitriles may be obtained from the corresponding ammoniacal salts, or from their amides, by the action of an excess of phosphoric anhydride, or of pentachloride of phosphorus :—in this way benzoate of ammonia may be converted into benzonitrile, since the latter contains the elements of benzoate of ammonia deprived of 4 atoms of water ; the hydrogen being supplied from the elements of the ammonia, whilst the oxygen is derived mainly from those of the acid :—

$$2\,\overbrace{PO_5}^{\substack{\text{Phosphoric}\\ \text{anhydride.}}}+\overbrace{H_4NO,C_{14}H_5O_3}^{\text{Benzoate of ammonia.}}=2\,(2\,HO,PO_5)+\overbrace{C_{14}H_5N}^{\text{Benzonitrile.}}.$$

$$PO_5+\overbrace{C_6H_5O_2,H_2N}^{\text{Propionamide.}}=2\,HO,PO_5+\overbrace{C_6H_5N}^{\text{Propionitrile.}}.$$

$$PCl_5+\overbrace{C_{14}H_5O_2,H_2N}^{\text{Benzamide.}}=2\,HCl+PCl_3O_2+\overbrace{C_{14}H_5N}^{\text{Benzonitrile.}}.$$

None of the nitriles hitherto procured contain oxygen, since all the salts which at present are known to yield them are formed either from monobasic acids of the form ($HO,C_xH_yO_3$), or from dibasic acids of the form ($2\,HO,C_xH_yO_6$).

The relations subsisting between benzoate of ammonia, benzamide, and benzonitrile, will exhibit the nature of the connexion between the ammonia salt, the amide, and the nitrile of a monobasic acid :—

$$\overbrace{H_4NO,C_{14}H_5O_3}^{\text{Benzoate of ammonia.}}-H_2O_2=\overbrace{H_2N,C_{14}H_5O_2}^{\text{Benzamide.}}\ (\text{or } C_{14}H_7NO_2)\,;$$

$$\text{and }\overbrace{H_2N,C_{14}H_5O_2}^{\text{Benzamide.}}-H_2O_2=\overbrace{C_{14}H_5N}^{\text{Benzonitrile.}}.$$

(1166) *Amidated Acids.*—If, instead of operating upon a *neutral* salt of ammonia, obtained from either a monobasic or a dibasic acid, any of the *acid* salts formed by ammonia with the dibasic acids be subjected to dehydration, a body is produced belonging to the class of *amidic*, or *amidated acids.* Balard in distilling binoxalate of ammonia thus obtained an azotised acid, which has been termed oxamic acid :—

$$\overbrace{H_4NO,HO,C_4O_6}^{\text{Acid oxalate of ammonia.}}=H_2O_2+\overbrace{HO,H_2N,C_4O_5}^{\text{Oxamic acid.}}.$$

This substance may serve as the type of a numerous class of compound acids, formed in a similar manner. The ammonia loses hydrogen, and the portion of the acid attached to the ammonia of the original salt loses oxygen, whilst that portion of acid which was attached to water as a base remains unaltered; so that oxamic acid may be viewed as a compound of unchanged oxalic acid and of oxamide:—

$$2\,\overbrace{(HO,H_2N,C_4O_5)}^{\text{Oxamic acid.}} = 2\,\overbrace{(H_2N)C_4O_4}^{\text{Oxamide.}} + 2\,\overbrace{HO,C_4O_6}^{\text{Oxalic acid.}}.$$

The amidic acids may also be obtained by acting upon the anhydride of a dibasic acid (1098) with dry ammonia in excess: the two bodies combine together, but the compound which is produced is found on examination to give evidence of the presence of but one half of the ammonia in the form of an ordinary ammoniacal salt; the second half having united with the elements of the acid to produce a new compound acid, which is the amidated acid of the one originally employed (Laurent). Thus, 1 molecule of anhydrous camphoric acid when acted upon by 1 of ammonia, yields 1 of hydrated camphoramic acid; the decomposition being supposed to consist in the conversion of one-half of the molecule of camphoric acid into camphoramide, while an atom of water is given off and enters into combination with the other half of the acid; these two bodies, camphoramide and hydrated camphoric acid then unite and form the new acid:—

$$\overbrace{C_{20}H_{14}O_6}^{\text{1 Mol. of camphoric anhydride.}} + H_3N = \underbrace{\overbrace{HO,C_{10}H_7O_3}^{\text{½ Mol. of hydrated camphoric acid.}} + \overbrace{H_2N,C_{10}H_7O_2}^{\text{½ Mol. of camphoramide.}}}_{\text{1 Mol. of hydrated camphoramic acid.}}.$$

This amidic acid may be converted into camphoramate of ammonia by causing it to unite with a second atom of ammonia.

The amidic acids may therefore be viewed as monobasic compounds derived from dibasic acids, in which one half of the group composing the original dibasic acid, is displaced by one half of the group which forms the amide of the acid; the combination of 1 molecule of the original dibasic acid with 1 of the amide furnishing 2 molecules of the monobasic amidic acid. To take again the case of the camphoric acid:—

$$2\,\overbrace{HO,C_{20}H_{14}O_6}^{\text{Hydrated camphoric acid.}} + \overbrace{(H_2N)_2C_{20}H_{14}O_4}^{\text{Camphoramide.}} = \overbrace{2\,(HO,H_2N,C_{20}H_{14}O_5)}^{\text{Hydrated camphoramic acid.}}.$$

When the aqueous solutions of the amidic acids are boiled, they quickly assimilate the elements of water, and become reconverted into acid salts of ammonia.

Hofmann regards the amidic acids as bodies formed upon the of hydrated oxide of ammonium, a substance too unstable to itself, but acquiring permanence when two atoms of its gen have been displaced by the radicle of a dibasic acid. we may compare oxamic acid with hydrated oxide of ammo- :—

$$\overbrace{\left.\begin{matrix}H_4N\\H\end{matrix}\right\}O_2}^{\text{Hydrated oxide of ammonium.}} \quad ; \quad \overbrace{(C_4O_4)''\left.\begin{matrix}H_2N\\H\end{matrix}\right\}O_2}^{\text{Oxamic acid.}}. \text{ (See also p. 51.)}$$

action of nitrous acid (NO_3) upon the amidated acids is cteristic: mutual decomposition occurs, one atom of each entering into the reaction, 2 atoms of nitrogen and one of are liberated, and the original acid from which the amidated ound was derived is reproduced. Aspartic acid (1144), for ple, may thus be reconverted into malic acid :—

$$2(\overbrace{HO,C_8H_6NO_7}^{\text{Aspartic acid.}})+(NO_3)_2=2(\overbrace{2\,HO,C_8H_4O_8}^{\text{Malic acid.}})+2\,N_2+H_2O_2.$$

1167) *Imides.*—Intermediates between the amides and the es there is a third class of bodies, the *imides*, which contain gen, and in which, if we are consistent, the existence of a termed *imidogen* HN (or ammonia less two equivalents of gen), must be assumed to exist. These compounds are not rous, but several of them are well known. They are obtained process of dehydration from certain acid salts of ammonia, from the amidated acids procurable from these salts; succinic, phoric, and phthalic acids, for instance, each yield amidic com- ds. The relation of these bodies to their respective acids be seen by the following comparison :—

Hydrated camphoric acid	$2\,HO,\ C_{20}H_{14}O_6$,
Acid camphorate of ammonia	$HO,H_4NO,C_{20}H_{14}O_6$,
Camphoramic acid (amidated camphoric acid)	$HO,H_2N,\ C_{20}H_{14}O_5$,
Camphorimide	$HN,\ C_{20}H_{14}O_4$.
Phthalic acid	$2\,HO,\ C_{16}H_4O_6$,
Acid phthalate of ammonia	$HO,H_4NO,C_{16}H_4O_6$,
Phthalamic acid (amidated phthalic acid) . .	$HO,H_2N,\ C_{16}H_4O_5$,
Phthalimide	$HN,\ C_{16}H_4O_4$.

Hence it will be perceived, that the imides are bodies formed the amidic acids by depriving these compounds of two equi- ts of water, just as the amidic acids are themselves obtained the acid salts of ammonia by depriving the latter of two valents of water :—

$$\overbrace{HO,H_4NO,C_{20}H_{14}O_6}^{\text{Acid camphorate of ammonia.}}=H_2O_2+\overbrace{HO,H_2N,C_{20}H_{14}O_5}^{\text{Hydrated camphoramic acid.}};\ \text{and}$$

$$\overbrace{HO,H_2N,C_{20}H_{14}O_5}^{\text{Hydrated camphoramic acid.}} = H_2O_2+\overbrace{HN,C_{20}H_{14}O_4}^{\text{Camphorimide.}}.$$

The theory of the existence of amidogen and imidogen as distinct organic groups or radicles in these different bodies, does not, upon a general view of the question, appear to have any strong probability. It was, indeed, proposed merely as a temporary expedient for representing the facts. The different groups designated as amides, imides, and nitriles, must rather be regarded as *residues*, the results of successive stages of dehydration. The terms themselves may, however, be conveniently retained, provided that their use be not taken to imply an adhesion to the theory in accordance with which these names were framed.

We may sum up the foregoing facts in the following manner. The compounds which correspond to the neutral ammonia salts are :—

1. The *amides*, produced by the combination of 1 atom of the hydrate of a monobasic acid with 1 atom of ammonia, and the elimination of water in the proportion of H_2O_2.

2. The *diamides*, produced by the combination of 1 molecule of the hydrated dibasic acid with 2 molecules of ammonia, attended by the separation of 2 H_2O_2.

3. The *nitriles*, produced by a combination of 1 molecule of a hydrated monobasic acid and 1 of ammonia, minus 2 H_2O_2; or from 1 molecule of the hydrate of a dibasic acid and 2 molecules of ammonia, minus 4 H_2O_2.

The compounds which correspond to the acid ammonia salts are :—

4. *Amidic acids*, formed from 1 molecule of the hydrate of a dibasic acid and 1 of ammonia, minus H_2O_2.

5. *Imides*, formed from 1 molecule of a hydrated dibasic acid and one of ammonia, with elimination of 2 H_2O_2.

(1168) *Hydramides.*—Besides the varieties of amides already mentioned, a particular class of compounds is formed by the action of ammonia upon certain volatile oils which appear to belong to the group of aldehyds. These bodies, termed *hydramides*, are furnished by the union of 3 molecules of the volatile oil and 2 molecules of ammonia, while water is separated in the proportion of 3 H_2O_2. Compounds of this kind are formed with the essential oils of bitter almonds, of spiræa, of cinnamon, of cummin, and of anise, as for example :—

$$3(\overbrace{C_{14}H_5O_2,H}^{\text{Hydride of benzoyl.}})+2\,H_3N=\overbrace{C_{42}H_{18}N_2}^{\text{Hydrobenzamide.}}+3\,H_2O_2.$$

$$3(\overbrace{C_{14}H_5O_4,H}^{\text{Hydride of salicyl.}})+2\,H_3N=\overbrace{C_{42}H_{18}N_2O_6}^{\text{Salhydramide.}}+3\,H_2O_2.$$

$$3(\overbrace{C_{16}H_7O_4,H}^{\text{Hydride of anisyl.}})+2\,H_3N=\overbrace{C_{48}H_{24}N_2O_6}^{\text{Anishydramide.}}+3\,H_2O_2.$$

Sulphuretted hydrogen in acting upon the hydramides, converts them into bodies analogous to the essences from which they were originally obtained, but the new essences contain as many equivalents of sulphur as they previously possessed of oxygen; thus, thiobenzol is obtained from benzhydramide, and thiosalicol from salhydramide:—

$$\overbrace{C_{42}H_{18}N_2}^{\text{Hydrobenzamide.}}\quad+3\,H_2S_2=2\,H_3N+3\,(\overbrace{C_{14}H_5S_2,\quad H}^{\text{Thiobenzol.}});$$

$$\overbrace{C_{42}H_{18}N_2O_6}^{\text{Salhydramide.}}+3\,H_2S_2=2\,H_3N+3\,(\overbrace{C_{14}H_5S_2O_2,H}^{\text{Thiosalicol.}}).$$

(1169) *Theory of the Amides.*—The amides, ever since their discovery, have offered interesting subjects of investigation and speculation to the chemist. They are substances which, although derived from ammonia, generally exhibit no basic power, and yet in certain cases they can be converted into compounds which possess all the properties of powerful alkalies. Although this subject is somewhat abstruse, we shall enter into it in some detail, in order to furnish some idea of the number and variety of the products which may be obtained by the methods of substitution from a body apparently so simple as ammonia, as well as to exemplify the great variety of methods in which it is possible and even necessary to pursue researches of this description.

The researches of Gerhardt and Chiozza (*Ann. de Chimie*, III. xlvi. 129) have shown that the amides bear the same relation to their respective acids that the volatile alkalies, methylia, ethylia, &c., do to the alcohols from which they are formed. The amides, when treated with nitrous acid, yield nitrogen and the acid from which the amide was obtained; and, under similar treatment, the volatile alkalies of the alcohols yield nitrogen and their corresponding alcohol. Upon this view, therefore, the amides are compounds derived by substitution from ammonia, upon which as a type they are founded; the ordinary amides of the monobasic acids, such as benzamide, being ammonia in which the basic character is neutralized by the substitution of an electro-negative radicle (such as benzoyl) for one of its atoms of hydrogen: thus, ammonia being $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, benzamide would be $(C_{14}H_7O_2N)$ or $\left.\begin{matrix}C_{14}H_5O_2\\H\\H\end{matrix}\right\}N$; and starting from this idea, Gerhardt was led to effect upon the amides a series of substitutions similar to those performed by Hofmann with ethylia and its homologues (1189). In this manner he was enabled by double decomposition to obtain amides, in which one atom, or two atoms of hydrogen were displaced by certain electro-negative bodies; these electro-negative bodies being compounds which when substituted for either one half or both halves of the hydrogen in the double atom of water, furnish in one case, the hydrated acids, in the other, the anhydrides (1096): benzoyl ($C_{14}H_5O_2$), for instance, when thus substituted for hydrogen, yields either benzoic acid or benzoic anhydride:—

$$\overbrace{\left.\begin{matrix}H\\H\end{matrix}\right\}O_2}^{\text{Water.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}O_2}^{\text{Benzoic acid.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}O_2}^{\text{Benzoic anhydride.}}.$$

The subject has been rapidly extended in the hands of other chemists, and an admirable summary of the whole is given by Hofmann (*Q. J. Chem. Soc.* xii. 62).

It has been already explained, that the various compounds formed upon a certain type may possess properties in which they gradually differ from those that precede and from those that follow them in the series; these differences depending upon the nature and number of equivalents of the elements or compounds which are introduced by processes of substitution into the prototype of the series (921). It becomes, therefore, quite possible to obtain compounds formed upon the type or plan of an eminently basic substance like ammonia, which, nevertheless, may possess neutral or even well-marked acid characters. In this manner various classes of amides have been formed by substitution, which may be distinguished thus:—

A. *Monamides*. B. *Diamides*. C. *Triamides*, formed respectively from one, from two, or from three atoms of ammonia. Each class admits of several subdivisions.

(1170) A. *Monamides*.—These are amides derived from a single atom of ammonia. They may be subdivided into 3 groups, according to the number of atoms of hydrogen in the ammonia which have been displaced by the electro-negative group. For instance, we have—

$$\overbrace{\left.\begin{matrix}A\\H\\H\end{matrix}\right\}N}^{\substack{\text{1. Primary}\\\text{monamides.}}} \quad ; \quad \overbrace{\left.\begin{matrix}A\\B\\H\end{matrix}\right\}N}^{\substack{\text{2. Secondary}\\\text{monamides.}}} \quad ; \quad \overbrace{\left.\begin{matrix}A\\B\\C\end{matrix}\right\}N}^{\substack{\text{3. Tertiary}\\\text{monamides.}}};$$

where A, B, and C represent the electro-negative groups by which the hydrogen is displaced.

The primary and secondary monamides are crystalline fusible bodies, for the most part volatile without decomposition at high temperatures. The tertiary monamides are in many cases liquid at ordinary temperatures, but they may be volatilized unaltered.

a. Primary Monamides.—These amides, like acetamide, $(C_4H_5O_2N) = \left.\begin{array}{c} C_4H_3O_2 \\ H \\ H \end{array}\right\} N$, represent a molecule of ammonia, in which a single atom of hydrogen is displaced by an equivalent organic radicle.*

The primary monamides may be prepared by various methods:—

1. They may be obtained by the simple distillation of the ammoniacal salts, in the manner practised by Dumas for procuring oxamide from oxalate of ammonia.

2. A better process consists in submitting to distillation a mixture of the potash salt with hydrochlorate of ammonia:—

$$\overbrace{\left.\begin{array}{c} C_{14}H_5O_2 \\ K \end{array}\right\} O_2}^{\text{Benzoate of potash.}} + \left.\begin{array}{c} H \\ H \\ H \end{array}\right\} N,HCl = \left.\begin{array}{c} H \\ H \end{array}\right\} O_2 + KCl + \overbrace{\left.\begin{array}{c} C_{14}H_5O_2 \\ H \\ H \end{array}\right\}}^{\text{Benzamide.}} O_2.$$

3. Liebig, in the preparation of the amides, takes advantage of the reaction which occurs when the compound ethers are mixed with ammonia, which may be employed in the form either of an aqueous or of an alcoholic solution. The result of this decomposition is the formation of an alcohol, and of the amide of the acid contained in the ether; for example:—

$$\left.\begin{array}{c} H \\ H \\ H \end{array}\right\} N + \overbrace{\left.\begin{array}{c} C_8H_7O_2 \\ C_4H_5 \end{array}\right\}}^{\text{Butyric ether.}} O_2 = \overbrace{\left.\begin{array}{c} C_8H_7O_2 \\ H \\ H \end{array}\right\}}^{\text{Butyramide.}} N + \overbrace{\left.\begin{array}{c} H \\ C_4H_5 \end{array}\right\}}^{\text{Alcohol.}} O_2.$$

This method is far superior to the first; it is of more general application, and the results which it yields are perfectly definite, being produced by a specific mode of double decomposition. Sometimes the reaction does not occur immediately; it may in such cases be facilitated by inclosing the ammonia and ether in a sealed tube, and exposing the mixture for some hours to a temperature of from 212° to 260°. In this manner benzamide is obtained speedily, although it requires many weeks at the ordinary temperature to effect the decomposition.

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* If a monobasic acid be defined to be an acid representing a double molecule of water $\left.\begin{array}{c} H \\ H \end{array}\right\} O_2$, in which 1 atom of hydrogen is displaced by an electro-negative radicle (acetic acid being $\left.\begin{array}{c} C_4H_3O_2 \\ H \end{array}\right\} O_2$), the primary amide is the amide derived from the normal ammonia salt of such an acid by the abstraction of 2 atoms of water.

4. Gerhardt and Chiozza prepare many of the amides with facility, by treating the solid sesquicarbonate of ammonia with the oxychlorides (1094) which correspond to the anhydrides (1096) of those acids of which the amides are required. This process is very advantageous when applied to the preparation of amides which are insoluble or sparingly soluble in water, such as benzamide and cuminamide: all that is required in the performance of the operation is to triturate the carbonate of ammonia in a mortar with the oxychloride; after which the amide is formed by gently warming the mass; carbonic acid escapes with effervescence, and the sal-ammoniac and excess of carbonate of ammonia are removed by washing with water. Cuminamide, for instance, is formed by the following reaction:—

$$\overbrace{2\,(C_{20}H_{11}O_2,Cl)}^{\text{Cuminic oxychloride.}} + \overbrace{4\,H_4NO, 3\,C_2O_4}^{\text{Sesquicarb. ammonia.}} = 2\left(\overbrace{\left.\begin{matrix}C_{20}H_{11}O_2\\ H\\ H\end{matrix}\right\}N}^{\text{Cuminamide.}}\right) + 3\,C_2O_4$$

$$+2\,\overbrace{H_4NCl}^{\text{Hydrochlor. ammonia.}} + 2\,H_2O_2.$$

Gaseous ammonia may be advantageously substituted in many cases for the carbonate; for example:—

$$\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N + H_3N + \overbrace{C_{16}H_7O_4,Cl}^{\substack{\text{Chloride}\\ \text{of anisyl.}}} = \overbrace{\left.\begin{matrix}C_{16}H_7O_4\\ H\\ H\end{matrix}\right\}}^{\text{Anisamide.}} N + H_3N,HCl.$$

5. In a similar manner the anhydrides of the monobasic acids are converted into monamides and a neutral salt of the acid, by the action of ammonia:—

$$\left.\begin{matrix}H\\ H\\ H\end{matrix}\right\}N + H_3N + \overbrace{\left.\begin{matrix}C_{18}H_7O_2\\ C_{18}H_7O_2\end{matrix}\right\}O_2}^{\substack{\text{Cinnamic}\\ \text{anhydride.}}} = \overbrace{\left.\begin{matrix}C_{18}H_7O_2\\ H\\ H\end{matrix}\right\}}^{\text{Cinnamide.}} N + \overbrace{\left.\begin{matrix}C_{18}H_7O_2\\ H_4N\end{matrix}\right\}O_2.}^{\substack{\text{Cinnamate}\\ \text{of ammonia.}}}$$

The monamides of acetic, propionic, butyric, valeric, and of a few other acids are freely soluble in water, and have a sweet taste; but the amides, as a class, are only sparingly soluble. Those which are soluble in water are also generally dissolved by alcohol and ether. By long boiling with water most of them become dissolved, and converted into ordinary salts of ammonia, by the assumption of the elements of water. This change is greatly accelerated by the addition of even a minute quantity of any free acid. The presence of a free alkali produces a like transformation; if potash or soda be the base employed, salts of these alkalies are formed, whilst ammonia is liberated: this change occurs very slowly at ordinary temperatures, but it takes place rapidly at the boiling point.

β. *Secondary Monamides.*—In these the displacement of hydrogen in the molecule of ammonia extends to two atoms. This class may be subdivided into two groups, according to the mode in which the substitution of hydrogen takes place; thus we have

(*a.*) Substitution of two atoms of a monatomic acid radicle belonging either to the same acid or to two different acids;

(*b.*) Substitution of a monatomic acid radicle, and of a monatomic alcohol radicle (secondary mixed monamides).

a. As an example of two different monacid radicles, we may take cumylsalicylamide* ($C_{34}H_{17}O_6N$), or $\left.\begin{matrix}C_{14}H_5O_4\\C_{20}H_{11}O_2\\H\end{matrix}\right\}N$; whilst diacetamide $C_8H_7NO_4 = \left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\\H\end{matrix}\right\}N$, offers an instance of displacement of two atoms of hydrogen by two of the same monacid radicle.

1. This subdivision of the secondary monamides may be prepared by heating the primary monamides to a certain temperature with an equivalent quantity of the electro-negative oxychloride: hydrochloric acid escapes in abundance, and the secondary monamide is found in the residue. Care must be taken to prevent the temperature from rising too high, otherwise nitriles are apt to be formed. If the products of the reaction assume a viscous form, they must not be dissolved whilst in this state, but must be allowed to become solid; their solidification may often be effected by the addition of a few drops of ether. The formation of cumylsalicylamide by treating chloride of cumyl with salicylamide, offers an instance of the formation of a secondary monamide in this manner:—

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_4\\H\\H\end{matrix}\right\}}^{\text{Salicylamide.}}N+\overbrace{\left.\begin{matrix}C_{20}H_{11}O_2\\Cl\end{matrix}\right\}}^{\text{Chloride of cumyl.}}=\overbrace{\left.\begin{matrix}C_{14}H_5O_4\\C_{20}H_{11}O_2\\H\end{matrix}\right\}N}^{\text{Cumyl-salicylamide.}}+\overbrace{\left.\begin{matrix}H\\Cl\end{matrix}\right\}}^{\text{Hydrochloric acid.}}.$$

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* The inharmonious and unwieldy names employed to designate these complicated substitution-products are apt to discourage the learner; but in the present state of chemical nomenclature they are almost necessary, for the purpose of pointing out the parentage and relationship of the bodies which they represent; since the compounds themselves have little or no intrinsic interest, the relations indicated being, in most cases, the really important circumstances.

2. Sometimes new amides may be obtained by heating together two primary amides in equivalent proportions; ammonia is then disengaged, and a secondary amide is formed. For example:—

$$\overbrace{\left.\begin{array}{c}C_{14}H_5O_2\\H\\H\end{array}\right\}}^{\text{Benzamide.}}N+\overbrace{\left.\begin{array}{c}C_{14}H_5O_4\\H\\H\end{array}\right\}}^{\text{Salicylamide.}}N=\overbrace{\left.\begin{array}{c}C_{14}H_5O_2\\C_{14}H_5O_4\\H\end{array}\right\}}^{\text{Benzoyl salicylamide.}}N+\overbrace{\left.\begin{array}{c}H\\H\\H\end{array}\right\}}^{\text{Ammonia.}}N.$$

3. In other cases they may be obtained by the action of hydrochloric acid upon 2 equivalents of a monamide; for example:—

$$2\overbrace{\left(\left.\begin{array}{c}C_4H_3O_2\\H\\H\end{array}\right\}N\right)}^{\text{Acetamide.}}+HCl=\overbrace{\left.\begin{array}{c}C_4H_3O_2\\C_4H_3O_2\\H\end{array}\right\}}^{\text{Diacetamide.}}N+\overbrace{H_3N,HCl.}^{\text{Hydrochlor. ammonia.}}$$

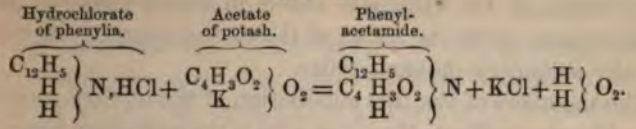
The members of the first subdivision of the secondary monamides possess the acid character more strongly than the primary monamides; and they frequently form metallic salts—those which contain silver being the salts most readily procured. Thus benzosulphophenylamide, when dissolved in boiling water by the aid of a few drops of ammonia, and mixed with a boiling solution of nitrate of silver, yields a compound in which silver takes the place of hydrogen in the original amide, the new silver salt crystallizing out in groups of colourless needles:—

$$\overbrace{\left.\begin{array}{c}C_{12}H_5,S_2O_4\\C_{14}H_5O_2\\H\end{array}\right\}N}^{\text{Benzosulphophenylamide.}}+\overbrace{\left.\begin{array}{c}NO_4\\Ag\end{array}\right\}O_2}^{\text{Nitrate of silver.}}=\overbrace{\left.\begin{array}{c}C_{12}H_5,S_2O_4\\C_{14}H_5O_2\\Ag\end{array}\right\}N}^{\text{Benzosulpho-phenylargentamide.}}+\overbrace{\left.\begin{array}{c}NO_4\\H\end{array}\right\}O_2.}^{\text{Nitric acid.}}$$

The prolonged action of the acids and alkalies, especially if aided by heat, expels the nitrogen of these secondary monamides, in the form of ammonia, and liberates the acids corresponding to the electro-negative radicles present in the compound.

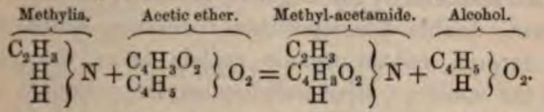
b. The second subdivision of the secondary monamides, in which one atom of hydrogen is displaced by a monacid radicle, and the second atom of hydrogen by an equivalent alcohol radicle, contains a large number of compounds which are represented by ethylacetamide, $C_8H_9NO_2=\left.\begin{array}{c}C_4H_3O_2\\C_4H_5\\H\end{array}\right\}N$. Compounds of this class may be formed by submitting the primary monammonias to the several processes which when applied to ammonia furnish the alcohol bases (1189), as well as by the following methods:—

1. *Distillation of the Salts of the Organic Acids with those of the Alcohol Bases.*



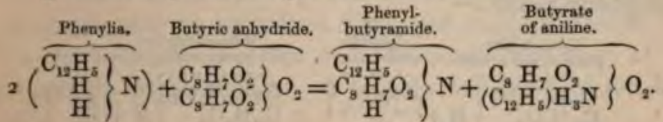
$$\overbrace{\left.\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right\}N,HCl}^{\text{Hydrochlorate of phenylia.}}+\overbrace{\left.\begin{matrix}C_4H_3O_2\\K\end{matrix}\right\}O_2}^{\text{Acetate of potash.}}=\overbrace{\left.\begin{matrix}C_{12}H_5\\C_4H_3O_2\\H\end{matrix}\right\}N}^{\text{Phenyl-acetamide.}}+KCl+\left.\begin{matrix}H\\H\end{matrix}\right\}O_2.$$

2. *Treatment of the Alcohol Bases with compound Ethers.*



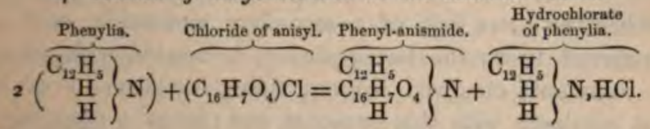
$$\overbrace{\left.\begin{matrix}C_2H_3\\H\\H\end{matrix}\right\}N}^{\text{Methylia.}}+\overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_5\end{matrix}\right\}O_2}^{\text{Acetic ether.}}=\overbrace{\left.\begin{matrix}C_2H_3\\C_4H_3O_2\\H\end{matrix}\right\}N}^{\text{Methyl-acetamide.}}+\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}.$$

3. *Action of the Anhydrides on the Alcohol Bases.*



$$2\Bigg(\overbrace{\left.\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right\}N}^{\text{Phenylia.}}\Bigg)+\overbrace{\left.\begin{matrix}C_8H_7O_2\\C_8H_7O_2\end{matrix}\right\}O_2}^{\text{Butyric anhydride.}}=\overbrace{\left.\begin{matrix}C_{12}H_5\\C_8H_7O_2\\H\end{matrix}\right\}N}^{\text{Phenyl-butyramide.}}+\overbrace{\left.\begin{matrix}C_8H_7O_2\\(C_{12}H_5)H_3N\end{matrix}\right\}O_2}^{\text{Butyrate of aniline.}}.$$

4. *Action of Oxychlorides on the Alcohol Bases.*



$$2\Bigg(\overbrace{\left.\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right\}N}^{\text{Phenylia.}}\Bigg)+\overbrace{(C_{16}H_7O_4)Cl}^{\text{Chloride of anisyl.}}=\overbrace{\left.\begin{matrix}C_{12}H_5\\C_{16}H_7O_4\\H\end{matrix}\right\}N}^{\text{Phenyl-anismide.}}+\overbrace{\left.\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right\}N,HCl}^{\text{Hydrochlorate of phenylia.}}.$$

The prolonged action of acids and of alkalies upon this class of mixed monamides gives rise to the reproduction of the acid and the base from which they were derived.

γ. *Tertiary Monamides.*—In these bodies the 3 atoms of hydrogen in ammonia are displaced by a corresponding number of radicles, one of which at least must be of an electro-negative character. This class may be subdivided into several groups, in which the following substitutions occur:—

(*a.*) Substitution of each atom of hydrogen by one of a monacid radicle;

(*b.*) Substitution of 2 atoms of hydrogen by acid radicles, and of the third atom of hydrogen by 1 atom of an alcohol radicle.

Hofmann regards the nitriles as belonging to the group of tertiary monamides in which the 3 atoms of hydrogen in the typical molecule of ammonia have been displaced by a *tribasic* acid radicle, and thus he represents the following compounds:—

Formio-nitrile or prussic acid .	$C_2HN=(C_2H)'''N$
Acetonitrile	$C_4H_3N=(C_4H_3)'''N$
Benzonitrile.	$C_{14}H_5N=(C_{14}H_5)'''N$;

but this mode of regarding the nitriles requires experimental confirmation.

a. Tertiary monamides containing 1 equivalent of an acid radicle and 2 equivalents of an alcohol radicle could doubtless be obtained by the action of the hydriodic ethers in excess upon the primary monammonias, or by the action of the electro-negative oxychlorides upon the secondary monammonias.

The members of the first subdivision of the tertiary monamides are readily prepared from the silver salts of the secondary monamides; for they are attacked by the negative oxychlorides even without the aid of heat, double decomposition occurring, whilst chloride of silver is formed, and an organic radicle takes the place of the silver in the amide. Benzosulphophenylargentamide is thus, by the action of chloride of benzoyl, readily converted into dibenzosulphophenylamide :—

$$\overbrace{\left.\begin{matrix}C_{12}H_5.S_2O_4\\C_{14}H_5O_2\\Ag\end{matrix}\right\}N}^{\substack{\text{Benzosulpho-}\\\text{phenylargentamide.}}}+\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right\}}^{\substack{\text{Chloride}\\\text{of benzoyl.}}}=\overbrace{\left.\begin{matrix}C_{12}H_5.S_2O_4\\C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}N}^{\substack{\text{Dibenzosulpho-}\\\text{phenylamide.}}}+\left.\begin{matrix}Ag\\Cl\end{matrix}\right\}.$$

When the silver salt of a secondary monamide, such as the one referred to in the last equation, is treated with ammonia, it is commonly dissolved without fixing the elements of water, but it combines with the ammonia and forms a diamide—that is to say, an amide derived from two molecules of ammonia; for example :—

$$\left.\begin{matrix}C_{12}H_5.S_2O_4\\C_{14}H_5O_2\\Ag\end{matrix}\right\}N+H_3N=\left.\begin{matrix}C_{12}H_5.S_2O_4\\C_{14}H_5O_2\\Ag\\H_3\end{matrix}\right\}N_2.$$

The other secondary and tertiary monamides when treated with ammonia have the power of fixing the elements both of ammonia and of water so as to form amidated acids, or rather salts of ammonia with amidated acids. Thus, for instance, benzosulphophenylamide may be transformed by ammonia into benzosulphophenylamate of ammonia :—

$$2\left(\left.\begin{matrix}C_{12}H_5.S_2O_4\\C_{14}H_5O_2\\H\end{matrix}\right\}N\right)+H_3N+2\,H_2O_2=(H_4NO,C_{52}H_{25}N_2S_4O_{15}).$$

b. Tertiary monamides of the second variety, in which 2 acid radicles and 1 alcohol radicle are present, are represented by ethyldiacetamide $C_{12}H_{11}NO_4=\left.\begin{matrix}C_4H_5\\C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}N$. They are usually obtained by acting upon the appropriate secondary monamide by an electro-negative oxychloride :—

$$\overbrace{\left.\begin{matrix}C_{12}H_5\\C_{14}H_5O_2\\H\end{matrix}\right\}}^{\text{Phenyl-benzamide.}} N+\overbrace{C_{14}H_5O_2.Cl}^{\text{Chloride of benzoyl.}}=\overbrace{\left.\begin{matrix}C_{12}H_5\\C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}}^{\text{Phenyldibenzamide.}} N+HCl.$$

Ethyldiacetamide has been obtained by acting upon cyanate of ethyl with acetic anhydride, a process which Hofmann considers as admitting of general application, and which he regards as the action of an anhydride upon a tertiary monammonia:—

$$\overbrace{\left.\begin{matrix}(C_2O_2)''\\C_4H_5\end{matrix}\right\}}^{\substack{\text{Cyanate of ethyl.}\\\text{(Ethylcarbonylamide.)}}} N+\overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}}^{\substack{\text{Acetic}\\\text{anhydride.}}} O_2=\overbrace{\left.\begin{matrix}C_4H_5\\C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}}^{\substack{\text{Ethyl-}\\\text{diacetamide.}}} N+C_2O_4.$$

The action of the alkalies upon these compounds reproduces the monammonias, and the acids from which the amide is derived:—

In a few instances metallic radicles occupy the place of the organic radicles in the amides. A primary monamide of this kind is obtained by heating potassium in ammonia, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N+K=\left.\begin{matrix}K\\H\\H\end{matrix}\right\}N+H$, and a similar compound of zinc is obtained by treating zinc-ethyl with ammonia, $2\left(\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\right)+\left(\begin{matrix}C_4H_5\\Zn\end{matrix}\right)_2=2\left(\left.\begin{matrix}Zn\\H\\H\end{matrix}\right\}N\right)+2\left(\begin{matrix}C_4H_5\\H\end{matrix}\right)$. And tertiary metallic monamides are exemplified in the case of copper and mercury, $(Cu_2)'_3N$, tricuprosamide, $H\bar{g}_3N$, trimercuramide: they are obtained by submitting the metallic oxides to the action of gaseous ammonia; $2\,H_3N+6\,CuO=(Cu_2)'_3N+3\,H_2O_2+N$.

(1171) B. *Diamides.*—These compounds are derived from two atoms of ammonia, and, like the monamides, may be subdivided into three principal groups, viz.:

$$\underset{\substack{\text{1. Primary}\\\text{diamides.}}}{\left.\begin{matrix}A_2\\H_2\\H_2\end{matrix}\right\}N_2}\quad;\quad\underset{\substack{\text{2. Secondary}\\\text{diamides.}}}{\left.\begin{matrix}A_2\\B_2\\H_2\end{matrix}\right\}N_2}\quad;\quad\underset{\substack{\text{3. Tertiary}\\\text{diamides.}}}{\left.\begin{matrix}A_2\\B_2\\C_2\end{matrix}\right\}N_2},$$

according as 2, 4, or 6 atoms of the hydrogen of the typical group has been displaced by a corresponding number of atoms of the substitution radicle. The last two of these principal groups again admit of various subdivisions.

a. The primary diamides are well represented by oxamide $C_4H_4N_2O_4=\left.\begin{matrix}(C_4O_4)''\\H_2\\H_2\end{matrix}\right\}N_2$; and to this class belong all the different varieties of urea (1414).

These diamides may in many instances be prepared by disti the normal ammonium salt, as was originally practised in the of oxamide itself. A better method consists in decomposin dibasic ether either by an alcoholic or an aqueous soluti ammonia in excess, for example :—

$$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2+\overbrace{\left.\begin{matrix}(C_8H_4O_4)''\\(C_4H_5)_2\end{matrix}\right\}O_4}^{\text{Succinic ether.}}=\overbrace{\left.\begin{matrix}(C_8H_4O_4)''\\H_2\\H_2\end{matrix}\right\}}^{\text{Succinamide.}}N_2+2\Big[\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}\Big].$$

The primary diamides may also be obtained by the acti ammonia on the anhydrides of the dibasic acids, for example

$$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2+\overbrace{(C_{20}H_{16}O_4)''O_2}^{\text{Camphoric anhydride.}}=\overbrace{\left.\begin{matrix}(C_{20}H_{16}O_4)''\\H_2\\H_2\end{matrix}\right\}}^{\text{Camphoramide.}}N_2+H_2O_2;$$

and it is probable that the action of ammonia on the oxychl of the dibasic acids would also yield the corresponding dia as in the formation of urea (carbamide) from ammonia and gene gas (chloride of carbonyl) :—

$$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2+2\,H_3N+\overbrace{(C_2O_2)''Cl_2}^{\text{Phosgene.}}=\overbrace{\left.\begin{matrix}(C_2O_2)''\\H_2\\H_2\end{matrix}\right\}}^{\text{Urea.}}N_2+2\,(H_3N,HCl).$$

The primary diamides are generally decomposed in measure when submitted to distillation. They are convert digestion with acids or with alkalies into ammonia and the d acids from which they are derived.

β. *The secondary diamides* contain the bodies often de as imides (1167), 4 atoms of hydrogen in the typical am group being displaced by 2 atoms of the radicle of a d acid.

A second group of the secondary diamides contains 1 at the radicle of a dibasic acid, and 2 atoms of a monobasic a radicle, or some corresponding hydrocarbon : diphenyl amide ($C_{32}H_{16}N_2O_4$) is an example of this class $\left.\begin{matrix}(C_8H_4O_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N$,

The diamides of this subdivision are obtained from alcoho by processes which, if applied to ammonia, would furnish p diamides ; for example :—

1. By distillation of the normal salts which the a form with dibasic acids :—

$$\overbrace{\left.\begin{matrix}(C_4\,O_4)''\\(C_{12}H_5,H_2N)_2\end{matrix}\right\}O_4}^{\text{Oxalate of phenylia.}}=2\,H_2O_2+\overbrace{\left.\begin{matrix}(C_4\,O_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2}^{\text{Diphenyloxamide.}}.$$

2. By the action of alcohol bases upon normal dibasic ethers :—

$$2\left(\overbrace{\left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}N}^{\text{Ethylia.}}\right)+\overbrace{\left.\begin{matrix}(C_4O_4)''\\(C_4H_5)_2\end{matrix}\right\}O_4}^{\text{Oxalic ether.}}=\overbrace{\left.\begin{matrix}(C_4O_4)''\\(C_4H_5)_2\\H_2\end{matrix}\right\}N_2}^{\text{Diethyloxamide.}}+2\left(\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}\right).$$

As well as by the action of the alcohol bases upon the anhydrides and oxychlorides of the dibasic acids.

The ureides (1415) belong to this subdivision of secondary diamides. They are obtained by the action of an oxychloride of a monobasic acid upon one of the varieties of urea; for example :—

$$\overbrace{\left.\begin{matrix}(C_2O_2)''\\H_2\\H_2\end{matrix}\right\}N_2}^{\text{Urea.}}+\overbrace{C_4H_3O_2,Cl}^{\text{Chloride of acetyl.}}=\overbrace{\left.\begin{matrix}(C_2O_2)''\\C_4H_3O_2)\\H_3\end{matrix}\right\}N_2}^{\text{Acetureide.}}+HCl.$$

γ. *The tertiary diamides* contain bodies derived from three atoms of the radicle of a dibasic acid, such as trisuccinamide $C_{24}H_{12}N_2O_{12}=\left.\begin{matrix}(C_8H_4O_4)''\\(C_8H_4O_4)''\\(C_8H_4O_4)''\end{matrix}\right\}N_2$; and in this group Hofmann proposes to include the hydramides, such as hydrobenzamide $C_{42}H_{18}N_2=\left.\begin{matrix}(C_{14}H_6)''\\(C_{14}H_6)''\\(C_{14}H_6)''\end{matrix}\right\}N_2$; but this supposition requires experimental support.

(1172) C. *Triamides.*—These compounds are derived from 3 atoms of ammonia; but they have not been extensively studied. Citryltriamide or citramide affords an example of a *primary triamide.* It may be obtained by the action of ammonia upon citric ether :—

$$\left.\begin{matrix}H_3\\H_3\\H_3\end{matrix}\right\}N_3+\overbrace{\left.\begin{matrix}(C_{12}H_5O_8)'''\\(C_4\,H_5)_3\end{matrix}\right\}O_6}^{\text{Citric ether.}}=\overbrace{\left.\begin{matrix}(C_{12}H_5O_8)'''\\H_3\\H_3\end{matrix}\right\}N_3}^{\text{Citramide.}}+3\left(\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}\right).$$

As an instance of a *secondary triamide,* phenylcitramide may be given; it may be obtained by acting upon phenylia (aniline) with citric acid :—

$$3\left(\overbrace{\left.\begin{matrix}C_{14}H_5\\H\\H\end{matrix}\right\}N}^{\text{Phenylia.}}\right)+\overbrace{\left.\begin{matrix}C_{12}H_5O_8\\H_3\end{matrix}\right\}O_6}^{\text{Citric acid.}}=\overbrace{\left.\begin{matrix}(C_{14}H_5)_3\\(C_{12}H_5O_8)'''\\H_3\end{matrix}\right\}N_3}^{\text{Phenylcitramide.}}+3\,H_2O_2.$$

Phosphorides, Arsides, Stibides.

There is every reason to anticipate the formation of a class of compounds corresponding to the amides, in which phosphorus, arsenic, or antimony occupies the place of the nitrogen of the amides. Indeed a *primary monophosphoride,* corresponding to a primary monamide, may be obtained by acting upon phosphuretted hydrogen with chloride of trichloracetyl :—

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P+\overbrace{C_4Cl_3O_2,Cl}^{\text{Chloride of trichloracetyl.}}=\overbrace{\left.\begin{matrix}C_4Cl_3O_2\\H\\H\end{matrix}\right\}}^{\text{Trichloracetyl phosphoride.}}P+HCl;$$

and a *tertiary monophosphoride,* corresponding to a tertiary monamide, has been obtained by acting upon phosphuretted hydrogen with chloride of benzoyl :—

$$\overbrace{\left.\begin{matrix}H\\H\\H\end{matrix}\right\}}^{\text{Phosph. hyd.}}P+3\,(\overbrace{C_{14}H_5O_2,Cl}^{\text{Chloride of benzoyl.}})=\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}}^{\text{Tribenzo-phosphoride.}}P+3\,HCl.$$

The organic radicles in these compounds often have their place supplied by the metals. They are generally formed by the action of phosphuretted, arseniuretted, or antimoniuretted hydrogen upon solutions of the metallic salts. Thus tricuprophosphide, Cu_3P, is obtained from nitrate of copper and phosphuretted hydrogen ; $H_3P+3\,(CuO,NO_3)=Cu_3P+3\,(HO,NO_5)$: tricuprarside from chloride of copper and arseniuretted hydrogen ; $H_3As+3\,CuCl=Cu_3As+3\,HCl$: and triargentostibide from nitrate of silver and antimoniuretted hydrogen; $H_3Sb+3\,(AgO,NO_5)=Ag_3Sb+3\,(HO,NO_5)$.

For a masterly discussion of the subject of amides and compound bases the reader is referred to Hofmann's paper on *Ammonia and its Derivatives* (*Q. J. Chem. Soc.* xi. 252).

The description of a few of the more interesting compounds belonging to the different classes of amides will suffice to give an idea of the general properties of these substances.

(*a*) *Monamides, or Amides of the Monobasic Acids.*

(1173) *Acetamide* $\left[\left.\begin{matrix}C_4H_3O_2\\H_2\end{matrix}\right\}N=C_4H_5NO_2\right]$.—This compound is obtained in abundance by exposing acetic ether with an equal volume of aqueous solution of ammonia, under pressure, for six hours to a temperature of 250° or 260°, then distilling the residue and collecting the distillate after the boiling point has risen to 430°. Acetamide forms a white solid which fuses at 172° and boils at 430°. It crystallizes in pearly leaflets after fusion. Acetamide is soluble in water and has a cooling sweetish taste. When distilled with phosphoric acid it loses two equivalents of water, and becomes converted into acetonitrile. If the acetic ether be decomposed by admixture with ethylia and exposure to heat in sealed tubes, it forms a corresponding compound, *ethyl-acetamide* or *aceto-ethylide* $C_8H_9NO_2 = \left.\begin{array}{l} C_4H_3O_2 \\ C_4H_5 \\ H \end{array}\right\} N$.

Ethyl-diacetamide, $C_{12}H_{11}NO_4 = \left.\begin{array}{l} 2\,(C_4H_3O_2) \\ C_4H_5 \end{array}\right\} N$, is a limpid, colourless, neutral liquid, which boils at 377°. It is obtained by heating cyanic ether with acetic anhydride to about 392°, in a sealed tube. Carbonic acid escapes on opening the tube when cold :—

$$\overbrace{C_4H_5O,C_2NO}^{\text{Cyanate of ethyl.}} + 2\,\overbrace{(C_4H_3O_3)}^{\text{Acetic anhydride.}} = C_2O_4 + \overbrace{C_{12}H_{11}NO_4}^{\text{Ethyldiacetamide.}}.$$

Trichloracetamide, $C_4H_2Cl_3NO_2 = \left.\begin{array}{l} C_4Cl_3O_2 \\ H_2 \end{array}\right\} N$, is the compound procured by decomposing trichloracetic ether with ammonia; but it is also obtained by acting upon several other perchlorinated ethylic ethers, such as the perchlorinated formic, carbonic, oxalic, and succinic ethers: perchloraldehyd likewise yields it when treated with ammonia. It is a crystallizable compound with a sweet taste; it melts at 275°, and is very soluble in alcohol and in ether.

(1174) *Propionamide* ($C_6H_7NO_2$), *Butyramide* ($C_8H_9NO_2$), and *Valeramide* ($C_{10}H_{11}NO_2$) may all be obtained by the action of ammonia, aided by heat, upon their respective ethers. They are fusible, volatile compounds, which may be sublimed without decomposition; they are soluble in water, alcohol, and ether. When distilled with phosphoric anhydride, they yield the nitriles of the acid, or the hydrocyanic ether of the alcohol below them :—

$$\overbrace{C_6H_7NO_2}^{\text{Propionamide.}} - H_2O_2 = \overbrace{C_6H_5N}^{\text{Propionitrile.}} \text{ (or } \overbrace{C_4H_5,C_2N}^{\text{Cyanide of ethyl.}}\text{);}$$

$$\overbrace{C_8H_9NO_2}^{\text{Butyramide.}} - H_2O_2 = \overbrace{C_8H_7N}^{\text{Butyronitrile.}} \text{ (or } \overbrace{C_6H_7,C_2N}^{\text{Cyanide of trityl.}}\text{);}$$

$$\overbrace{C_{10}H_{11}NO_2}^{\text{Valeramide.}} - H_2O_2 = \overbrace{C_{10}H_9N}^{\text{Valeronitrile.}} \text{ (or } \overbrace{C_8H_9,C_2N}^{\text{Cyanide of tetryl.}}\text{).}$$

(1175) *Benzamide* ($C_{14}H_7NO_2$) is a white solid, fusible at 239°, which may be sublimed without undergoing decomposition. It is sparingly soluble in cold water; boiling water dissolves it easily, and deposits it, on cooling, in acicular crystals. It is still more readily dissolved by alcohol and by ether, from which it crystallizes in right rhomboidal prisms. When boiled with free acid or alkali, it is quickly converted into benzoate of ammonia. Benzamide is most easily obtained by the action of dry ammoniacal gas upon chloride of benzoyl; in which case it is accompanied by the formation of benzonitrile. It may also be procured by heating an alcoholic solution of ammonia with benzoic ether for some hours in a sealed tube. When boiled with red oxide of mercury, water is separated, and *hydrargo-benzamide* is obtained; $2\ C_{14}H_7NO_2 + Hg_2O_2 = 2\ C_{14}H_6HgNO_2 + H_2O_2$. Hydrargo-benzamide may be viewed as $\left.\begin{matrix} C_{14}H_5O_2 \\ Hg \\ H \end{matrix}\right\}N$, or benzamide in which the second typical atom of hydrogen has been displaced by mercury. Benzamide, when heated with potassium, loses oxygen; hydrogen is eliminated and benzonitrile is formed:—

$$2\ C_{14}H_7NO_2 + K_2 = 2\ C_{14}H_5N + H_2 + 2\ (KO,HO).$$

(*b*) *Nitriles.*

(1176) *Benzonitrile* ($C_{14}H_5N$): *Sp. gr. of liquid* 1·007; *of vapour* 3·70.—This substance is a colourless oil, with a powerful odour of bitter almonds. It is sparingly soluble in water, but is miscible with alcohol and ether in all proportions. It boils at 376°, and emits an inflammable vapour, which burns with a smoky flame. It may be obtained by the dry distillation of benzoate of ammonia, or of benzamide; and still more readily by mixing either of these bodies with phosphoric anhydride in excess before proceeding to the distillation; the distillate when washed with hydrochloric acid, and re-distilled, is pure benzonitrile. Benzamide also yields benzonitrile when treated with chloride of benzoyl:—

$$\overbrace{C_{14}H_7NO_2}^{\text{Benzamide.}} + \overbrace{C_{14}H_5O_2Cl}^{\text{Chloride of benzoyl.}} = \overbrace{C_{14}H_5N}^{\text{Benzonitrile.}} + \overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}} + HCl.$$

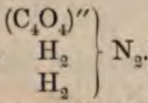
Benzonitrile, when boiled with alkalies, or with concentrated acids, is converted into benzoic acid and ammonia, with assimilation of the elements of water.

Cumonitrile ($C_{20}H_{11}N$; *Sp. gr. of liquid* 0·765) may be obtained by similar methods from cuminate of ammonia. It has a fragrant odour, and boils at 462°.

The nitriles of the fatty acids are identical with the hydrocyanic ethers of the alcohol in the series immediately below that of the acid from which they are obtained (1000).

(c) *Diamides—Amides of Dibasic Acids.*

The dibasic acids give rise to the formation of diamides; that is to say, to amides formed from 2 equivalents of ammonia. We shall examine those of two acids only, viz., the amides of oxalic acid and those of succinic acid. The latter afford an instructive illustration of the preparation and properties of primary, secondary, and tertiary diamides, from the same acid.



(1177) *Oxamide*, $(H_2N)_2C_4O_4 = \left.\begin{array}{c}(C_4O_4)''\\ H_2\\ H_2\end{array}\right\} N_2$.]—This interesting compound is most readily obtained by decomposing oxalic ether by an aqueous or an alcoholic solution of ammonia. It may also be procured, though less advantageously, by distilling oxalate of ammonia, when it condenses in the neck of the retort and in the receiver in the form of white flocculi. Oxamide is a light tasteless powder, which is insoluble in cold water, but soluble to a small extent in boiling water, from which it is deposited on cooling in crystalline flakes. The solution is neutral, and gives no precipitate with salts of lime. It is insoluble in alcohol. It may be sublimed in an open tube, though with difficulty. When its vapour is transmitted through a red-hot tube, it is decomposed, according to Liebig, into bicarbonate of ammonia, hydrocyanic acid, oxide of carbon, and urea:—

$$\overbrace{2\,[(H_2N)_2C_4O_4]}^{\text{Oxamide.}} = \overbrace{H_3N,C_2O_4}^{\text{Bicarb. ammon.}} + H,C_2N + C_2O_2 + \overbrace{H_4N_2C_2O_2}^{\text{Urea.}}.$$

When oxamide is heated to 436°, in a sealed tube with water, it becomes transformed into oxalate of ammonia. The same change is effected by boiling oxamide with dilute acids or alkalies. If heated alone in closed vessels to 590°, it is converted into a mixture of cyanogen, oxide of carbon, and carbonate of ammonia. Oxamide, in fact, contains the elements of cyanogen and water; $(H_2N)_2C_4O_4 = (C_2N)_2 + H_2O_2$; but the water reacting upon a portion of oxamide, converts it into oxalate of ammonia, and this, by the action of heat, is resolved into carbonate of ammonia and oxide of carbon:—

$$\overbrace{(H_2N)_2C_4O_4}^{\text{Oxamide.}} + 2\ H_2O_2 = \overbrace{2\ H_4NO,C_4O_6}^{\text{Oxalate of ammonia.}};\ \text{and}$$

$$\overbrace{2\ H_4NO,C_4O_6}^{\text{Oxal. ammonia.}} = \overbrace{2\ H_4NO,C_2O_4}^{\text{Carb. ammonia.}} + C_2O_2.$$

When oxamide is boiled with red oxide of mercury, the two bodies enter into combination, and form a white heavy powder $[HgO,(H_2N)_2C_4O_4]$.

If oxalic ether be decomposed by the alcohol alkalies, such as ethylia, methylia, and amylia, or by other bases, such as aniline, compounds are obtained corresponding to oxamide: thus ethylia, when made to act upon oxalic ether, yields diethyloxamide, $(C_{12}H_{12}N_2O_4) = \left.\begin{matrix}(C_4O_4)''\\(C_4H_5)_2\\H_2\end{matrix}\right\}N_2$; and aniline, under similar circumstances, if heated in a closed tube to 320°, produces diphenyloxamide (oxanilide), $C_{28}H_{12}N_2O_4$:—

$$\overbrace{2\ C_4H_5O,C_4O_6}^{\text{Oxalic ether.}} + \overbrace{2\ (C_{12}H_5,H_2N)}^{\text{Aniline.}} = \overbrace{\left.\begin{matrix}(C_4\ O_4)''\\(C_{12}H_5)_2\\H_2\end{matrix}\right\}N_2}^{\text{Oxanilide.}} + \overbrace{2\ (C_4H_5O,HO)}^{\text{Alcohol.}}.$$

(1178) *Succinamide* $\left(C_8H_8N_2O_4 = \left.\begin{matrix}(C_8H_4O_4)''\\H_2\\H_2\end{matrix}\right\}N_2\right)$.—When succinic ether is mixed with twice its volume of a concentrated solution of ammonia, alcohol is liberated, and succinamide is deposited in the form of a granular crystalline compound. It is nearly insoluble in cold water, but is dissolved by boiling water in considerable quantity. Alcohol and ether do not dissolve it.

Succinimide, or *disuccinamide* $[2(C_8H_5NO_4 + 2\ Aq) = 2(C_8H_4O_4)H_2N_2 + 4\ Aq]$.—The simplest method of procuring this compound consists in neutralizing a solution of succinic acid with ammonia, evaporating to dryness, and submitting the residue to distillation. It may also be obtained by causing dry ammonia to react upon succinic anhydride; during this reaction water is formed, and a considerable elevation of temperature occurs:—

$$\overbrace{2\ C_8H_4O_6}^{\text{Succinic anhydride.}} + 2\ H_3N = \overbrace{\left.\begin{matrix}(C_8H_4O_4)''\\(C_8H_4O_4)''\\H_2\end{matrix}\right\}N_2}^{\text{Disuccinamide.}} + 2\ H_2O_2.$$

When succinamide is heated, ammonia is evolved, and succinimide is formed :—

$$\overbrace{2\,C_8H_8N_2O_4}^{\text{Succinamide.}} = 2\,H_3N + \overbrace{C_{16}H_{10}N_2O_8}^{\text{Succinimide.}}.$$

At a temperature above 400° it sublimes without decomposition, and may be purified, by crystallization, from its solution in boiling water, which on cooling deposits it in beautiful, efflorescent, rhombic tables. It is freely soluble in water, and the solution has a feebly acid reaction; alcohol also dissolves it, but it is insoluble in ether; it fuses at 410°. Succinimide is metameric with succinamic acid. It yields a crystallizable compound with silver, termed *succinimidate of silver*, $\left.\begin{matrix}C_8H_4O_4\\ C_8H_4O_4\\ Ag_2\end{matrix}\right\}N_2$, [$= 2\,C_8H_4AgNO_4$]; this body is obtained in needles by mixing a boiling concentrated alcoholic solution of succinimide, rendered slightly alkaline by ammonia, with a hot alcoholic solution of nitrate of silver: the salt is deposited as the liquid cools. It is not decomposed by potash in the cold, but on the application of heat to the mixture ammonia is evolved. Succinimidate of silver is freely soluble in ammonia, and if the solution so obtained be left to spontaneous evaporation, a syrupy alkaline liquid is left, which gradually becomes converted into a mass of rectangular prisms [$2C_8H_4AgNO_4$, $2\,H_3N$], from which potash immediately liberates ammonia. Succinimidate of silver is decomposed with explosion when suddenly heated: it is isomeric with succinamate of silver, into which it is converted if its ammoniacal solution be boiled for some time; it then becomes much more soluble, and is no longer explosive.

Trisuccinamide $C_{24}H_{12}O_{12},N_2 = (C_8H_4O_4)''_3N_2$.—When 10 parts of succinic oxychloride (1131) are dissolved in twice their volume of ether, and mixed with 27 parts of the succinimidate of silver, an immediate reaction occurs, sufficient heat is emitted to volatilize the ether, and chloride of silver is formed :—

$$\overbrace{(C_8H_4O_4)_2Ag_2N_2}^{\text{Succinimidate of silver.}} + \overbrace{C_8H_4O_4Cl_2}^{\text{Succinic oxychloride.}} = \overbrace{(C_8H_4O_4)_3N_2}^{\text{Trisuccinamide.}} + 2\,AgCl.$$

Boiling ether dissolves it under pressure, and deposits small crystals, which are fusible at 181°. Water and alcohol decompose this compound, alcohol converting it into succinimide without the formation of succinic ether.*

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* Wurtz has put forward a view of the amides differing from the foregoing one, inasmuch as he proposes to consider the monobasic amides as formed

(*d*) *Amidated Acids.*

(1179) A single instance will sufficiently illustrate the nature of these bodies, after what has been already stated of their general properties: but the existence of this class of substances is not confined to the compounds of organic chemistry, since both sulphuric and carbonic acids yield amidated acids, viz., the sulphamic and carbamic acids; these bodies being produced by the reaction of dry ammonia upon anhydrous sulphuric, and carbonic acids; the compounds to which the term of ammonides was applied (507) being supposed by Laurent and Gerhardt to be amidated salts of ammonia.

Oxamic Acid ($C_4H_3NO_6=HO,H_2N,C_4O_5$).—When binoxalate of ammonia is exposed to a carefully regulated heat, it loses its water of crystallization, and begins to undergo decomposition at a temperature of about 430°, giving off water, carbonic acid, formic acid, and carbonic oxide. The residue in the retort, if not heated too strongly, consists of oxamide and an acid substance soluble in

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from the type of the double molecule of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$, and thus to connect them with the acids: for example, if acetic acid in its hydrated form be written $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$, the amides of acetic acid would be thus indicated:—

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}HN}^{\text{Acetamide.}}\quad;\quad\overbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}(C_4H_5)N}^{\text{Ethylacetamide.}}\quad;$$

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}HN}^{\text{Diacetamide.}}\quad;\quad\overbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}(C_4H_5)N.}^{\text{Ethyldiacetamide.}}$$

It will be seen that upon this theory the amides are supposed to be formed by the action of ammonia upon the hydrated acids; H_3N losing two atoms of hydrogen, which combine with the two exterior atoms of oxygen, while the residue HN takes the place of the oxygen thus removed.

Wurtz considers, with Gerhardt, that the dibasic acids are derived from two double molecules of water (1099), and their relation to their amides and amidated acids admits of being very simply traced: for example—

$$\overbrace{\left\{\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}O_2\\\left.\begin{matrix}H\\H\end{matrix}\right\}O_2\end{matrix}\right\}}^{\text{Water.}}\;;\;\overbrace{\left.\begin{array}{cl}H & \}\,O_2\\(C_4O_4)'' & \\H & \}\,O_2\end{array}\right\}}^{\text{Oxalic acid.}}\;;\;\overbrace{\left.\begin{array}{cl}H & \}\,HN\\(C_4O_4)'' & \\H & \}\,HN\end{array}\right\}}^{\text{Oxamide.}}\;;\;\overbrace{\left.\begin{array}{cl}H & \}\,O_2\\(C_4O_4)'' & \\H & \}\,HN\end{array}\right\}}^{\text{Oxamic acid.}}.$$

This view is ingenious, but it does not account for the fact that oxamide is neutral, and that oxamic acid is monobasic, whilst oxalic acid is intensely acid and dibasic. The two atoms of hydrogen which are here represented as occupying similar positions in oxalic acid, in oxamide, and in oxamic acid in each case, certainly perform the functions of a base in oxalic acid; if the theory be correct, they also must occupy a basic position in the other compounds, and as such should be exchangeable with a metal: but on making the experiment this exchange is found not to take place.

This soluble compound is oxamic acid. It may be lized by baryta water, or by lime water, and yields crystalline f these bases on evaporating the solution. If its aqueous n be boiled, it is reconverted into binoxalate of ammonia; $_2N,C_4O_5+H_2O_2=HO,H_4NO,C_4O_6$. Oxamic acid may be ore readily prepared by decomposing an alcoholic solution lic ether by an alcoholic solution of ammonia in excess; de is formed, and in a day or two the liquid deposits crystals nethane mixed with those of oxamate of ammonia. The latter e separated from the oxamethane by dissolving the mixture two substances in hot alcohol, adding an alcoholic solution oride of calcium, and separating the sparingly soluble te of lime by filtration.

large number of dibasic acids form compounds analogous to acid, such as the following:—

Sulphamic Acid . .	HO,H_2N,S_2O_5.
Carbamic Acid . .	HO,H_2N,C_2O_3.
Tartramic Acid . .	$HO,H_2N,C_8H_4O_9$.
Malamic Acid . . .	$HO,H_2N,C_8H_4O_7$.
Phthalamic Acid . .	$HO,H_2N,C_{16}H_4O_5$.
Camphoramic Acid .	$HO,H_2N,C_{20}H_{14}O_5$.

ido-acids, of which amido-benzoic (benzamic) is the reprere, will be considered hereafter. (1246, 1424).

§ II. THE ORGANIC BASES.

80) The ALKALOIDS, or *organic alkalies*, are not less numean the organic acids: they form a natural group of high t to the chemist, not only on account of their remarkable ition, but also from their powerful effects as medicinal or us agents upon the animal economy.

the majority of instances the natural organic bases are from the vegetable kingdom, and constitute the active le of the plant that contains them. They always occur in ation with some acid, which is also frequently of organic , and peculiar to the plant or family of plants in which it is In many cases the alkaloids which occur in one species of family are found also in several of the other members of family.

egetable bases when in solution have generally a decidedly action upon test papers, and for the most part they neutralize the acids, forming definite and well crystallized salts.* They obey the usual law of bases when their salts are submitted to electrolytic analysis; since under these circumstances the base is liberated at the platinode of the voltaic battery. Most of these bases are dissolved sparingly by water, but are more freely soluble in alcohol, especially when it is at a boiling temperature; the alcoholic solutions as they cool generally deposit the alkaloids in the crystalline form. Some of these bases occur in two isomeric conditions, one of which is crystallizable, and the other amorphous; both forms combine with acids in the same proportion, but the crystalline variety alone yields crystalline salts.

The vegetable or organic bases may be subdivided into two well-marked classes:—1st. Those which, like aniline ($C_{12}H_7N$), do not contain oxygen:—and 2nd. Those which, like quinia ($C_{40}H_{24}N_2O_4+6\ Aq$), do contain it. The bases of the first class are oily and volatile; they absorb oxygen rapidly from the air: this class has recently been augmented by the formation of numerous artificial alkaloids, many of which closely resemble aniline in properties, and may, like aniline, be regarded as derivatives of ammonia. Less is known of the derivation and rational composition of the second and more complicated class of oxidized bases.

All of the volatile bases have a powerful odour; they may be distilled either alone or with the vapour of water, without undergoing decomposition. Advantage is taken of this property in their preparation or extraction; it is sufficient to digest the plant containing them in a weak alkaline ley, and to submit the mixture to distillation. A portion of ammonia always comes over with the condensed products, which are neutralized by sulphuric acid, then evaporated, and afterwards digested with alcohol. This menstruum leaves the sulphate of ammonia, but dissolves the sulphate of the organic base, which may be purified by recrystallization. If this salt be agitated with a mixture of equal parts of a strong solution of hydrate of potash and ether, the mixture separates on standing into two layers, the upper one consisting of an ethereal solution of the volatile base. If this ethereal solution be decanted, and placed in a retort and distilled, the ether is first expelled, and the may afterwards be obtained in a state of purity in the last ns which pass over.

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* It is much to be regretted that a uniform system of nomenclature has not been adopted for these compounds; that the termination *ia*, for example, as in morphia and strychnia, has not been appropriated to the bases, to indicate their analogy with ammonia: the termination *ine*, might then have been restricted to the neutral principles. Both these terminations are now attached indifferently, by many writers, to the bases, and it might be attended with inconvenience were the attempt uniformly made to alter the termination familiarized by usage. In this work I have generally indicated the neutral bodies, such as salicin, amygdalin, &c., by the termination *in*, reserving the ending, *ine*, for those which have basic properties.

he general process of extracting the alkaloids which are not le is simple. The rasped or powdered vegetable is digested dilute sulphuric or hydrochloric acid, by which the organic f the alkaloid is decomposed, and a more soluble sulphate or ide is formed. To the filtered solution, ammonia, magnesia, arbonate of soda is added, by which a copious precipitate of pure alkaloid is occasioned; and this, if magnesia be used, gled with the excess of this earth, and often with an inso- compound of the organic acid with magnesia. The pre- te is treated with boiling alcohol, from which, on cooling, kali generally crystallizes: it is redissolved in sulphuric or chloric acid, digested with animal charcoal, and the salt is d by recrystallization. Animal charcoal, though it perfectly es the colour, has in many cases, however, the serious dis- tage of retaining also a large proportion of the salt of the e alkali; and if a great excess of charcoal be used, almost ole of the salt may be withdrawn from the solution.

the search for an organic base in cases of suspected poison- one of these substances, Stas recommends the adoption of lowing method (*Chem. Gaz.*, 1852, 350):—To the contents stomach add twice their weight of pure concentrated alcohol, om 10 to 30 grains of tartaric acid, and heat the mixture sk to 160° or 170°; allow it to cool completely; filter, and the residue with strong alcohol. Evaporate the filtrate *in* r in a current of air at a temperature not exceeding 90°, g the solution if any fat separates; treat the dry residue ld absolute alcohol; evaporate *in vacuo;* dissolve the acid in a few drops of water, adding bicarbonate of potash or ll it ceases to produce effervescence; then agitate with 4 es its bulk of pure ether. When clear, allow a portion of thereal solution to evaporate spontaneously in a very dry in this way the base is obtained in a state of purity sufficient w of its examination by its characteristic reagents. If sul- acid be added to the ethereal solution, the sulphates of the ng volatile bases may be separated in the crystalline form— ia, tetrylia, nicotylia, aniline, quinoline, and picoline; sul- ylia is slightly soluble in ether. Stas states that he has fully isolated morphia, codeia, strychnia, brucia, veratria, ia, hyoscyama, aconitina, and colchinia, all of which, ned with acid, are sufficiently soluble in ether to tion by the foregoing method.

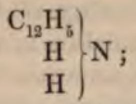
Many of the organic bases are also dissolved by chloroform, which may often be advantageously substituted for ether in Stas's process. The liquid is filtered, if necessary, and agitated with about one-thirtieth of its bulk of chloroform; the chloroform speedily separates in the form of a heavy oily layer, which can be decanted; it will be found to contain nearly the whole of the base, which may afterwards be purified by the usual methods. The following bases are especially soluble in chloroform—viz., veratria, quinia, brucia, narcotine, atropia, and strychnia; cinchonia is but sparingly soluble, and morphia still less so.

(1181) *Nature of the Organic Bases.*—The composition of the vegetable alkalies is remarkable; all of them contain nitrogen, and in the greater number each atom of base includes one atom of nitrogen. Berzelius regarded ammonia as the compound which confers upon them their basic character; and he considered them to be compounds of ammonia with a variety of neutral principles, which in most cases are not susceptible of isolation; the union of the neutral principle or *colligate* with the ammonia being of the same intimate nature as that of alcohol with sulphuric acid in the sulphethylic acid, where neither of the constituents exhibits its ordinary characters. Thus quinia ($C_{20}H_{12}NO_2 + 3\,Aq$; halving the formula now adopted) was represented by Berzelius as $(C_{20}H_9O_2,H_4NO) + 2\,Aq$, or as a compound of the colligate, $C_{20}H_9O_2$, with oxide of ammonium and water of crystallization. This mode of viewing the composition of certain vegetable bases acquires some support from the discovery that, by the direct union of ammonia with a limited class of neutral substances, such as oil of mustard, and oil of bitter almonds, a number of basic compounds may be obtained, which present a striking analogy both in composition and properties to many of the organic bases produced by living plants: but this theory of Berzelius is now generally abandoned.

A different view was suggested several years ago by Liebig, who, finding that these bases gave no evidence of the presence of ammonia ready formed within them, suggested that they might be compounds containing H_2N, or amidogen; and that they might be derivatives from ammonia, in which an atom of hydrogen had been displaced by an equivalent organic group: he even predicted that if it should be found possible to displace this atom of hydrogen by ethyl, or by some electro-negative hydrocarbon, a powerful volatile base would probably be obtained. This sagacious conjecture has since been fully verified by the discoveries of Wurtz and Hofmann, who have succeeded in obtaining the very compounds anticipated by Liebig; and Hofmann, as we have already seen, has extended the process of substitution much further. Liebig's view, with the extension and modifications required by the progress of discovery in this direction, admits in many instances of being happily applied to the natural vegetable bases, since these bodies themselves can be subjected to operations analogous to those which are applied in the formation of the alcohol bases; and portions of the hydrogen which they contain may thus be displaced by basic hydrocarbons: for instance, conylia $[(C_{16}H_{14})''H,N]$ may be converted into ethyl-conylia $[(C_{16}H_{14})''C_4H_5, N]$, by displacing an atom of hydrogen by an equivalent of ethyl. The number of exchangeable atoms of hydrogen in the different bases depends upon the molecular constitution of the particular base under experiment (1189, 1190).

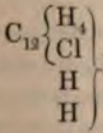
But the hydrocarbons either originally existing in the base or subsequently introduced into it, may also experience a change in their components by a species of secondary substitution by chlorine or bromine, whilst the general basic properties of the compound remain unchanged. Aniline $(C_{12}H_5,H_2N)$ for example, may be represented as ammonia in which one atom of hydrogen is displaced by $C_{12}H_5$ (phenyl); but aniline may lose a part of its hydrogen, and receive chlorine in its place, without having its basic character destroyed, becoming chloraniline $(C_{12}H_4Cl,H_2N)$: and even NO_4 may be substituted for a portion of the hydrogen in aniline, while the new body (nitraniline, $C_{12}H_4NO_4,H_2N$) still retains its power of forming salts with acids. Nitraniline affords an instance of the artificial formation of an alkaloid containing two atoms of nitrogen; and examples of the occurrence of bases which contain more than one atom of nitrogen without any corresponding increase in basic power are not wanting among the products of organic nature. The relations of aniline to chloraniline and nitraniline, may be represented in the following manner:—

Aniline . . . . . .



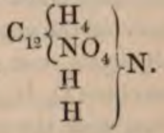
$$\left.\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right\}N;$$

Chloraniline.



$$C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\left.\begin{matrix}\\\\H\\H\end{matrix}\right\}N;$$

Nitraniline .



$$C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right.\left.\begin{matrix}\\\\H\\H\end{matrix}\right\}N.$$

Hofmann, in the course of his researches upon aniline, discovered another method of combination which is worthy of remark, since it explains a second *mode in* which an additional atom of nitrogen may be introduced into the alkaloid without increasing its basic power:—cyanogen unites directly with aniline, forming a body, the composition of which is represented by $C_{14}H_7N_2$, but which is evidently not a hydrocyanate of aniline, for this would be represented by the formula $C_{12}H_7N,HC_2N$; nor is it a substitution-product formed by the displacement of 1 atom of hydrogen by an equivalent of cyanogen; but a new body, *cyaniline*, which possesses basic properties, and enters into combination with acids in the proportion of one equivalent of acid to each equivalent of aniline which the new base contains.*

It is evident that changes such as these affect that portion only of the compound which, like $C_{12}H_5$ in aniline, has been introduced into the ammonia by substitution; the compound retaining the basic power which it originally derived from the ammonia, upon the type of which it has been constructed. When this type is destroyed, the basic power of the compound disappears. For example, just as oxalate of ammonia, by the abstraction of the elements of four atoms of water, loses its saline character, and becomes converted into an indifferent insoluble body, oxamide,—and this by the further abstraction of four more atoms of water furnishes cyanogen (1164); so oxalate of aniline, by losing four atoms of water, becomes oxanilide; and by abstraction of four more atoms of water becomes oxanilo-nitrile, or phenylo-cyanogen, which still retains an atom of nitrogen intimately combined both with carbon and hydrogen, but which has lost its relationship or homology with ammonia, and with it has also lost its basic character. Thus:—

$$\overbrace{(C_{12}H_5,H_3NO)_2C_4O_6}^{\text{Oxalate of aniline.}} = \overbrace{(C_{12}H_5,HN)_2C_4O_4}^{\text{Oxanilide.}} + 2\ H_2O_2;\ \text{and}$$

$$\overbrace{(C_{12}H_5,HN)_2C_4O_4}^{\text{Oxanilide.}} = \overbrace{(C_{12}H_4,NC_2)_2}^{\text{Phenylocyanogen.}} \quad + 2\ H_2O_2.$$

(1182) *Analogy of Organic Bases with Ammonia.*—The remarkable parallelism in properties of the salts of the organic bases with those of ammonia, will be rendered still more evident by the following additional particulars:—

Many of the vegetable bases may be obtained, like ammonia, in the anhydrous state: such, for instance, are cinchonia $C_{40}H_{24}N_2O_2$, and strychnia $C_{42}H_{22}N_2O_4$; and the same is the case almost without exception with the aniline class. These anhydrous bases combine

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* Bases will be described hereafter, which, like guanidine and methyluramine (1420), appear to be formed upon the polyatomic type, and are derived from 2 or 3 atoms of ammonia united into one group.

ith the hydracids like ammonia, and do not require any
f the elements of water; hydrochlorate of cinchonia,
le, consists of ($C_{40}H_{24}N_2O_2$,2 HCl): but, as is the case
ammonia, whenever these bases unite with the oxyacids,
atom of monobasic acid with which the alkali unites,
f water is required for the production of the salt, or 2
vater for every atom of dibasic acid. Sulphate of cinchonia,
ice, which contains ($C_{40}H_{24}N_2O_2$,2 HO,S_2O_6+8 Aq), loses
of water of crystallization by heat, but the remaining 2
nnot be expelled without decomposing the salt. The
lts which the organic bases form, also closely resemble
sponding compounds of ammonia:—for example, with
e of platinum they yield yellow crystalline double chlorides
g solubility. These compounds are of considerable im-
to the chemist, since they furnish him with very accurate
f determining the equivalent number of the organic base.
ide of gold likewise forms with them similar compounds,
ofmann has proposed to employ for the same purpose.
the organic bases also furnish nearly insoluble white pre-
when their solutions are mixed with one of corrosive
e, or with a solution of iodide of mercury in iodide of
n. They yield extremely insoluble compounds with
molybdate of soda: and a solution of the mixed sulphates
and persulphate of iron, yields by spontaneous evapora-
tals having the octohedral form of alum (Will). Octo-
rystals are also obtained when a solution of sulphate
a, which is an analogue of ammonia, is mixed with one of
te of alumina, and left to spontaneous evaporation.

ddition to these compounds there are some others peculiar
ass of bodies. Solutions of salts of the vegetable bases
ost part, when mixed with biniodide of potassium, yield
es insoluble in water, but soluble in boiling alcohol,
ich they crystallize on cooling. It has been proposed to
compounds in determining the bases quantitatively for
ses of analysis. With this object the precipitate formed
niodide is placed in very dilute sulphuric acid and treated
ments of zinc; iodide of zinc and protiodide of the base
ed; and on the addition of ammonia in excess, the orga-
is precipitated, whilst the zinc is retained in solution.
cases it is found preferable to throw down both the oxide
nd the alkali by means of carbonate of ammonia; the
e after washing with water is treated with boiling alcohol,
olves out the alkali, leaving the oxide of zinc; and on

evaporating the alcoholic solution, the alkali is obtained in a state of purity.

Nearly all the organic bases form insoluble curdy precipitates with gallotannic acid: indeed, this acid is one of the most complete precipitants of the vegetable alkalies. These gallotannates, when heated, melt to a resinous mass, and are soluble to some extent in boiling water; they are also dissolved freely by boiling alcohol.

The action of tartaric acid upon the vegetable bases is analogous to that which it exerts on many of the inorganic bases: for instance, the tartrates of iron, of copper, and of some other metals, are not precipitated by the addition of the alkalies to their aqueous solutions; but tartrate of lead is decomposed with separation of the metallic oxide. So it is with many of the organic bases; the tartrates of brucia, of quinia, and of morphia, are not precipitated by an excess of potash or of soda; by converting these organic bases into tartrates and adding an excess of an alkaline solution, they may be separated from strychnia, cinchonia, and narcotine, the tartrates of which are decomposed in the usual way on the addition of potash or of ammonia.

The greater number of the vegetable bases, when in solution, produce the phenomenon of left-handed rotation on a ray of polarized light. The artificial bases in general do not possess the power of affecting a polarized ray (Laurent). The left-handed rotation exerted by narcotine becomes right-handed when this base is combined with acids; and, generally speaking, the effect of the addition of an acid to the base is to reduce its power of rotation, though with quinia the rotatory power is exalted by the addition of an acid.

Artificial Formation of Organic Bases.

(1183) It has already been stated that many organic bases may be prepared by artificial means. All attempts at obtaining those which occur naturally in plants have, however, hitherto been unsuccessful. The following are the principal processes resorted to for the purpose of preparing organic bases artificially:—

1. By destructive distillation of organic bodies containing nitrogen.

2. By distillation of the organic alkalies with hydrate of potash (Gerhardt); and of the cyanic ethers with hydrate of potash (Wurtz).

3. By combination of ammonia with certain volatile oils, and

subsequent moderate heating of the product with solution of potash (Fownes).

4. By reduction of nitrous derivatives of the hydrocarbons by means of sulphuretted hydrogen (Zinin).

5. By substitution of the alcohol radicles for hydrogen in ammonia, during the action of hydrobromic or hydriodic ethers upon ammonia (Hofmann).

6. By substitution of the alcohol radicles for hydrogen in phosphuretted, arseniuretted, and antimoniuretted hydrogen, by means of processes analogous to those last mentioned.

1. *Destructive Distillation of Substances containing Nitrogen.*—This method constitutes the foundation of the manufacture of ammonia, which is always the principal basic substance thus furnished; but since the ammonia is, during this operation, brought into contact with hydrocarbons and with other products of distillation, in their nascent state, the elements of the ammonia react upon these bodies, and produce a small quantity of other bases, homologous with, or derivable from, ammonia. In the preparation of coal-gas, for instance, four, at least, of these compounds come over along with the coal-tar: these are aniline, or kyanol ($C_{12}H_7N$); picoline, a base metameric with aniline; quinoline, or leukol ($C_{18}H_7N$); and pyridine ($C_{10}H_5N$). Stenhouse has shown that when vegetable matters rich in nitrogen, such as the seeds of the *Leguminosæ* and of the *Cerealia*, are distilled in a similar way in vessels excluded from the air, in addition to ammonia, large quantities of volatile oily bases come over, the nature of which varies with that of the compound distilled (*Phil. Trans.*, 1850): and the destructive distillation of bones furnishes an empyreumatic oily liquid, known as *Dippel's oil*, which contains a variety of analogous bases.

2. *Action of Potash on Organic Bodies.*—Sometimes the azotised matters, instead of being distilled alone, are mixed with hydrate of potash, and submitted to the action of heat. In this way aniline is abundantly obtained from indigo, and quinoline from quinia and cinchonia; quinoline is also obtained by similar means, though in smaller proportion, from strychnia. Greville Williams finds that some other volatile bases, including pyridine and several of its homologues, are formed at the same time. Although, therefore, the following equations do not represent the whole of the reaction which occurs under these circumstances, they will serve to point out the simple relation between quinoline and the complex bases which furnish it by distillation:—

$$\overbrace{C_{40}H_{24}N_2O_2}^{\text{Cinchonia.}}+3\,H_2O_2=2\,(\overbrace{C_{18}H_7N}^{\text{Quinoline.}})+2\,\overbrace{C_2O_4}^{\text{Carb. acid.}}+8\,H_2;$$

$$\overbrace{C_{40}H_{24}N_2O_4}^{\text{Quinia.}}+2\,H_2O_2=2\,(C_{18}H_7N)+2\,C_2O_4+7\,H_2;$$

$$\overbrace{C_{42}H_{22}N_2O_4}^{\text{Strychnia.}}+4\,H_2O_2=2\,(C_{18}H_7N)+3\,C_2O_4+8\,H_2.$$

In like manner aniline is obtained from isatin:—

$$\overbrace{C_{16}H_5NO_4}^{\text{Isatin.}}+2\,H_2O_2=\overbrace{C_{12}H_7N}^{\text{Aniline.}}+2\,C_2O_4+H_2.$$

The carbonic acid produced during these operations remains in combination with the potash, whilst the hydrogen escapes. It was by distilling the cyanic and cyanuric ethers with hydrate of potash that Wurtz discovered the remarkable bases, methylia, ethylia, and amylia; the reaction being analogous in all these cases (1011):—

$$\overbrace{C_4H_5O,C_2NO}^{\text{Cyanic ether.}}+2\,(KO,HO)\quad=\overbrace{C_4H_5,H_2N}^{\text{Ethylia.}}+2\,\overbrace{KO,C_2O_4}^{\text{Carb. potash.}}.$$

If ethylate of potash (KO,C_4H_5O, potassium-alcohol) be substituted for hydrate of potash, a more advanced substitution-product may be obtained:—

$$\overbrace{C_4H_5O,C_2NO}^{\text{Cyanic ether.}}+2\,\overbrace{(KO,C_4H_5O)}^{\text{Ethylate potash.}}=\overbrace{(C_4H_5)_3N}^{\text{Triethylia.}}\;+2\,\overbrace{KO,C_2O_4}^{\text{Carb. potash.}}.$$

3. Another process consists in combining ammonia with the aldehyds. This may be effected by distilling the combinations of the aldehyds with bisulphite of ammonia, with hydrated alkalies or with soda-lime. Thus the compound with acetic aldehyd furnishes dimethylia (C_4H_7N): that of œnanthylic aldehyd trihexylia ($C_{36}H_{39}N$); and that of oil of cinnamon triphenylia ($C_{36}H_{15}N$) (Hofmann). The decompositions cannot be represented by a general equation. Certain of the volatile oils which possess the properties of aldehyds, also combine with ammonia when digested with it. The compound obtained in this manner exhibits in some cases, without further treatment, the properties of an alkaline base; but in other instances a neutral body is formed, which, when treated with a solution of potash, is converted into an isomeric substance, possessed of basic powers. An example of the first kind occurs when the oil of mustard is treated with ammonia: it thus forms a powerful crystalline base, which, when mixed with acids, at once unites with them, and furnishes crystallizable salts:—

$$\overbrace{C_8H_5NS_2}^{\text{Oil of mustard.}}+H_3N \text{ becoming } \overbrace{H_3(C_6H_5)N_2,C_2S_2}^{\text{Thiosinamine.}}\,;$$

phuretted urea of the allyl series: whilst an instance of
d kind is afforded by bitter almond oil, which, on uniting
aonia in the proportion of 3 atoms of the oil and 2 atoms
nia, loses 6 atoms of water, and forms the neutral body,
zamide:—

$$3\,\overbrace{C_{14}H_6O_2}^{\text{Oil of bitter almonds.}}+2\,H_3N=\overbrace{C_{42}H_{18}N_2}^{\text{Hydrobenzamide.}}+3\,H_2O_2.$$

ese crystals of hydrobenzamide are boiled with a solution
e potash for some hours, they are gradually converted into
e (amarine), an alkaline body insoluble in water, which has
e composition as hydrobenzamide, and forms beautiful
h acids. In a similar manner Fownes prepared furfurine
g with potash on the compound of furfurol and am-
—

$$3\,\overbrace{C_{10}H_4O_4}^{\text{Furfurol.}}+2\,H_3N=2\,\overbrace{C_{15}H_6NO_3}^{\text{Furfuramide.}}+3\,H_2O_2\,;$$
$$\text{and } 2\,\overbrace{C_{15}H_6NO_3}^{\text{Furfuramide.}}=\overbrace{C_{30}H_{12}N_2O_6}^{\text{Furfurine.}}.$$

fourth process for obtaining organic bases artificially is
arkable one invented by Zinin. Many compounds of
nd hydrogen, such as benzol, toluol, and naphthalin, when
ith strong nitric acid, lose an atom of hydrogen, whilst
lent of peroxide of nitrogen (NO_4) takes its place. In this
ol is converted into nitrobenzol:—

$$\overbrace{C_{12}H_6}^{\text{Benzol.}}+HO,NO_5=\overbrace{C_{12}H_5NO_4}^{\text{Nitrobenzol.}}+H_2O_2\,;$$

$_4H_8$ into nitrotoluol ($C_{14}H_7NO_4$), and naphthalin ($C_{20}H_8$)
onaphthalin ($C_{20}H_7NO_4$). These new compounds are
n alcohol; and Zinin found that, after saturating the
solution with dry ammoniacal gas, and then transmitting
ted hydrogen, the solution, if left to itself, deposited sul-
ater was formed at the same time, whilst the whole of
en was removed from the original compound, and a new
e, possessed of basic characters, was found in the solu-
his substance in many instances might be obtained in
n evaporation. Nitrobenzol is thus converted into ani-
otoluol into toluylia, and nitronaphthalin into naphthylia;
—

$$\overbrace{C_{12}H_5NO_4}^{\text{Nitrobenzol.}}+3\,H_2S_2=\overbrace{C_{12}H_5,H_2N}^{\text{Aniline.}}+2\,H_2O_2+3\,S_2;$$

$$\overbrace{C_{14}H_7NO_4}^{\text{Nitrotoluol.}}+3\,H_2S_2=\overbrace{C_{14}H_7,H_2N}^{\text{Toluylia.}}+2\,H_2O_2+3\,S_2;$$

$$\overbrace{C_{20}H_7NO_4}^{\text{Nitronaphthalin.}}+3\,H_2S_2=\overbrace{C_{20}H_7,H_2N}^{\text{Naphthylia.}}+2\,H_2O_2+3\,S_2.$$

In each case the whole of the sulphur is precipitated,
atoms of hydrogen enter into the combination instead
atoms of oxygen which are removed. The object of ad
monia in the first instance is merely to retain the sul
hydrogen in solution, so that the reaction may have tim
place. A large number of new bases have already bee
by this process, and numbers of others will, no doubt
covered. Béchamp has shown that by treating nitrobe
other nitrous derivatives of the hydrocarbons, with prot
iron, they are reduced; the protoxide of iron becomes c
into sesquioxide, and is most of it precipitated in the f
basic sesquiacetate of iron, whilst an organic base is form
method is even preferable to Zinin's:—

$$\overbrace{C_{12}H_5NO_4}^{\text{Nitrobenzol.}}+12\,\overbrace{(FeO,\overline{Ac})}^{\text{Protacet. of iron.}}+H_2O_2=\overbrace{C_{12}H_7N}^{\text{Aniline.}}+6\,\overbrace{Fe_2O_3,\ 12\,\overline{A}}^{\text{Basic peracet. of}}$$

All the bases thus procured are destitute of oxyge
resemble ammonia in their mode of combination with oxy
atom of water being essential to the formation of these sa
phate of toluylia, for example, consists of $2(HO,C_{14}H_9N)S$
Liebig and Wöhler have also formed two bases, term
dine ($C_{12}H_{13}NS_4$), and *selenaldine* ($C_{12}H_{13}NSe_4$), in which
and selenium are constituent elements. They are proc
the reducing agency of sulphuretted hydrogen and selen
hydrogen respectively, upon an aqueous solution of 3
aldehyd-ammonia: thus in the case of thialdine:—

$$3\,(\overbrace{C_4H_4O_2,\ H_3N}^{\text{Aldehyd ammonia.}})+3\,H_2S_2=\overbrace{C_{12}H_{13}NS_4}^{\text{Thialdine.}}+2\,H_4NS+3\,H_2O_2$$

These alkalies belong to the groups of nitrile bases (1190)
5 and 6. These important processes admit of vario
fications, which will be considered when speaking of the n
bases which have been obtained by their application (118

In a few instances new bases are formed by processes o
tion from other bases, as cotarnine and narcogenine from n
(1210), cacotheline from brucia (1205), and methyluram
kreatine (1420).

tly, the formation of organic bases has been observed during es of fermentation and putrefaction ;—the putrefaction of a flour, for example, furnishing trimethylia, ethylia, and

84) The following order will be observed in the description h of the organic bases as, from their important applications, bearing upon other groups, or from the mode of their forma- em most worthy of notice :—

A. *Artificial Bases.*

Bases which do not contain oxygen :—
  a. Aniline series $(C_{2n}H_{2n-7})H_2N$;
  b. Pyridine series $(C_{2n}H_{2n-5})'''N$;
  c. Quinoline series $C_{2n}H_{2n-11})'''N$.
Bases obtained by the action of ammonia on derivatives of cohols.
Bases derived from phosphuretted hydrogen.
Polyatomic bases.
Bases obtained by the action of ammonia upon certain tial oils.

B. *Natural Bases.*

Volatile oily bases destitute of oxygen :—
  Conylia ;—Nicotylia ;—Sparteia.
Oxidized bases :—
  a. Bases from the cinchonas ;
  b. Bases from opium ;
  c. Bases from pepper ;
  d. Bases from the strychnos tribe ;
  e. Other less known bases ;
  f. Caffeine and Theobromine.

A. ARTIFICIAL BASES.

1. *Volatile Bases which do not contain Oxygen.*

a. Aniline Series $(C_{2n}H_{2n-7})'H_2N$.

8 ANILINE, *Kyanol, Phenylamine, Phenylia, Crystalline,* $(C_{12}H_7N=C_{12}H_5,H_2N=93)$; *Sp. gr. of liquid* 1·020 : ·210 ; *Boiling pt.* 360°—This remarkable base may be a several sources, and by a variety of reactions :—

ntained in small quantity among the products of the llation of coal in the process of gas-making.

2. Nitrobenzol is converted by hydrosulphate of ammonia into aniline and water, whilst sulphur is deposited :—

$$C_{12}H_5NO_4+3\,H_2S_2=C_{12}H_5,H_2N+2\,H_2O_2+3\,S_2.$$

A similar reduction takes place under the influence of a mixture of zinc and hydrochloric acid, or of protacetate of iron. In the latter case much of the aniline comes over in the form of acetate. The pasty mass which is the result of the reaction is best distilled by the heat of a bath containing a concentrated solution of chloride of calcium. Aniline is now manufactured by these methods on a large scale for the dyer.

3. It is also furnished by the distillation, with lime, of nitrotoluol, or of its metamerides, salicylamide and anthranilic acid, all of which substances furnish aniline and carbonic acid ; thus :—

$$\overbrace{C_{14}H_7NO_4}^{\text{Nitrotoluol.}} = C_2O_4+\overbrace{C_{12}H_5,H_2N}^{\text{Aniline.}}.$$

The product from salicylamide is always accompanied by carbolic acid ($HO,C_{12}H_5O$).

4. One of the methods by which aniline is easily procured consists in mixing finely-powdered indigo with a concentrated solution of hydrate of potash, and submitting it to distillation: the mass swells up greatly, and water holding ammonia in solution passes over, accompanied by aniline in the form of a brownish oil. This oil, when re-distilled, furnishes pure aniline, amounting to nearly one fifth of the weight of the indigo.

This base is a colourless, limpid liquid, of an agreeable vinous odour and an aromatic burning taste. It is very acrid and poisonous. Aniline remains fluid at −4°. When dropped upon paper it produces a greasy stain, which, owing to the volatility of the base, speedily disappears. Aniline is a non-conductor of electricity ; it refracts light powerfully. When exposed to the air it absorbs oxygen rapidly, and becomes converted into a brown, resinous mass ; it is, therefore, necessary to distil it in a current of hydrogen, or of carbonic acid. It also distils over easily along with the vapour of water, when solutions of its salts are mixed with an excess of potash and submitted to distillation. Aniline is heavier than water, in which it is soluble to a considerable extent ; but on saturating the liquid with certain salts, such as chloride of sodium or sulphate of magnesia, the aniline is separated. Aniline has little or no action on test papers ; it may be dissolved in unlimited quantity by alcohol, ether, and wood spirit.

Most of the salts of aniline crystallize readily. They are *colourless*, but if exposed to the air while moist, they become rose-

deal be plunged into a solution of any of
ually acquires an intense yellow colour. If an
of a salt of aniline be mixed with a solution of
deep blue colour is produced, which gradually
dirty red. With chromic acid these salts strike a
or a black colour, according to the degree of con-
the solutions.* Aniline produces a white precipitate
of corrosive sublimate, and a green crystalline pre-

---

in has obtained from aniline a beautiful purple colour, now
loyed as a dye-stuff, giving a tint known as *Mauve*. In order to
irects (*Chemical News*, June 8th, 1861) equivalent proportions
aniline and bichromate of potash to be brought into solution,
wed to stand until the reaction is complete. The black pre-
ed upon a filter till free from sulphate of potash. It is then
sted in coal naphtha, as long as it takes up any brown colour.
then dissolved in alcohol, and on evaporation is left tolerably
purple is but sparingly soluble in cold water, to which it
purple colour. Hot water, and water slightly acidulated, dis-
eely; alkalies precipitate it. With corrosive sublimate and
forms insoluble blue or purple compounds. Oil of vitriol
a sulphuric acid dissolve it, forming a dirty green solution,
blue on dilution, and on further dilution resumes its original
g nitric acid destroys it, as also does chlorine; concentrated
n of potash does not decompose it.

d with peroxide of lead and sulphuric acid, aniline furnishes a
our, which Dr. D. Price has called *roseine*.

Magenta is another extremely beautiful colouring matter.
oxidation from aniline. If anhydrous bichloride of tin be
to excess of aniline, the two bodies combine. The pasty mass
eated gradually, stirring all the time. It becomes brown,
iling point almost black, but it is of a rich crimson when
ayers. The temperature is kept up for some time. It is then
a large quantity of water, which gradually dissolves out the
, leaving the tin as a protosalt. On saturating the solution
lt, the colouring matter is separated as a mass of pitchy con-
ay be purified from adhering resin by means of benzol.
ies of feeble oxidizing power—such as corrosive sublimate,
y, arsenic acid, &c.—may be substituted for bichloride of tin
n of fuchsine. Fuchsine, according to Perkin, is an organic
repared from bichloride of tin, is obtained in the form of
$_2$O,HCl? Béchamp), and from nitrate of mercury in that of
ia precipitates fuchsine from its salts as a bulky red powder.
ydrochloric or sulphuric acid, forming a brownish-yellow
h ammonia precipitates the dye unaltered. Excess of the
uchsine, forming nearly colourless liquids: it is but sparingly
oderately soluble in alcohol, insoluble in ether and hydro-
holic solution when evaporated leaves it in films which
bly beautiful golden green metallic reflection.

s, known as *bleu de Paris*, has also been obtained by acting
h temperatures with bichloride of tin in closed vessels.

line dyes from their aqueous but not acidulated solutions
ature of 120° to 140°. Perkin uses tannin as a mordant
r upon cotton and calicoes, working in acid solutions of the
basic lead salt may also be used as a mordant. In calico-
are usually mixed with albumen, which by coagulation
s the colour on the fibre.

cipitate in one of chloride of copper. Both precipitates contain aniline in combination with the metallic chlorides.

When a solution of hydrochlorate of aniline is mixed with one of nitrite of silver, nitrogen escapes in abundance, whilst carbolic acid is separated in oily drops; this decomposition is due to the reaction of nitrous acid on aniline:—

$$2\,\overbrace{C_{12}H_7N}^{\text{Aniline.}} + 2\,NO_3 = 2\,\overbrace{(HO,C_{12}H_5O)}^{\text{Carbolic acid.}} + 2\,N_2 + H_2O_2.$$

Aniline acts powerfully upon the hydriodic ethers of the different alcohols, in the manner already explained (1027), and yields derived bases, such as ethylaniline $[(C_4H_5,C_{12}H_5,H)N]$. When mixed with the oxychlorides, or with the anhydrides, of the organic acids, aniline yields compounds which correspond with the amides. With acetic oxychloride, for instance, it produces acetanilide, and hydrochlorate of aniline:—

$$\overbrace{\left.\begin{matrix}C_4H_3O_2\\ Cl\end{matrix}\right\}}^{\text{Acetic oxychloride.}} + 2\,\overbrace{C_{12}H_7N}^{\text{Aniline.}} = \overbrace{\left.\begin{matrix}C_4\,H_3O_2\\ C_{12}H_5\\ H\end{matrix}\right\}N}^{\text{Acetanilide.}} + \overbrace{C_{12}H_7N,HCl.}^{\text{Hydrochlorate of aniline.}}$$

Aniline forms anilidated acids, anilides, dianilides, and aniles. The aniles correspond to the imides of the ammonia group; they contain the elements of 1 molecule of a hydrate of a dibasic acid and 1 of aniline, minus water, in the proportion of 2 H_2O_2. The anilidated acids, which correspond to the amidated acids, are formed from 1 molecule of a dibasic acid and 1 of aniline, with the separation of 2 H_2O_2. The compounds enumerated in the following list afford examples of each of these classes of substances:—

Anilides.

Formanilide	$C_{12}H_5,HN,C_2\,H\,O_2$
Acetanilide	$C_{12}H_5,HN,C_4\,H_3O_2$
Benzanilide	$C_{12}H_5,HN,C_{14}H_5O_2$
Cinnamanilide	$C_{12}H_5,HN,C_{18}H_7O_2$.

Dianilides.

Oxanilide	$(C_{12}H_5)_2,H_2N_2,C_4O_4$
Succinanilide	$(C_{12}H_5)_2,H_2N_2,C_8H_4O_4$
Suberanilide	$(C_{12}H_5)_2,H_2N_2,C_{16}H_{12}O_4$.

Anilidated Acids.

Sulphanilic acid	$HO,C_{12}H_5,HN,S_2\,O_5$
Oxanilic acid	$HO,C_{12}H_5,HN,C_4\,O_5$
Succinanilic acid	$HO,C_{12}H_5,HN,C_8\,H_4\,O_5$
Camphoranilic acid	$HO,C_{12}H_5,HN,C_{20}H_{14}O_5$.

Aniles.

le . . . . . . $C_{12}H_5N,C_8\,H_4\,O_4$
nile . . . . . . $C_{12}H_5N,C_{20}H_{14}O_4$.

($C_{12}H_5,HN,C_4H_3O_2$) may be taken as the repre-
class of anilides. It is easily prepared by acting
ith oxychloride of acetyl, which is to be added drop
aniline as long as decomposition ensues. Hydro-
ine is formed, and may be removed by washing the
ater: acetanilide remains in the form of a yellowish
resinoid appearance which may be obtained in
ant prismatic crystals, by dissolving it in hot water
ne liquid to cool; alcohol and ether also dissolve it.
°·6, and solidifies to a crystalline mass, on cooling.
stilled without decomposition. When fused with
is liberated.

mbines directly with cyanogen, and forms a feeble
yaniline ($C_{14}H_7N_2$), which is easily obtained by trans-
rent of cyanogen in excess through a solution of
nol; it contains the elements of 1 equivalent of
of cyanogen. It may be procured in beautiful
rystals by recrystallization from hot alcohol: when
ids it is very unstable.

remarkable as yielding compounds possessed of basic
n portions of the hydrogen are displaced by chlorine
The first two of these compounds are best obtained
g chlorisatin and dichlorisatin, by means of hydrate
57). Trichloraniline is procured by acting upon
ns of chlorine, which converts the aniline at first
compound, and then into a sticky tar-like mass;
trichlorophenic acid ($HO,C_{14}H_2Cl_3O$) is formed at
but the trichloraniline may be obtained in a state
distilling the mixture with a solution of potash,
the acid, while trichloraniline passes over and is
elicate needles.

e ($C_{12}H_4Cl,H_2N$) is a weaker base than aniline,
in white, fusible, volatilizable, crystalline needles:
strong disposition to crystallize; and, like those
impart a yellow colour to a slip of deal. *Dichlo-*
Cl_2N) is still less basic in its characters than the
tance; and *trichloraniline* ($C_{12}H_4Cl_3N$) is a very
line compound, which is entirely devoid of basic
The corresponding compounds with bromine, in

general properties closely resemble the chlorinated forms of aniline.

The action of chlorine in these cases is very interesting: although the introduction of a single equivalent of this body into the composition of aniline does not destroy the basic character, yet the electro-negative power of chlorine is exhibited in the diminution of the basic energy possessed by the new group, as compared with that of aniline; each successive addition of chlorine weakening the basic property, until it disappears altogether in trichloraniline.

Hofmann, by whom these bases were discovered, has also succeeded, in conjunction with Muspratt, in preparing a yellow crystalline compound which fuses at 226°, and may be sublimed unaltered. This substance is termed *a nitraniline*, $C_{12}H_4NO_4$, H_2N; it is procured by the reduction of dinitro-benzol by means of hydrosulphate of ammonia. This body also forms salts with acids; it contains an equivalent of peroxide of nitrogen in the place of an atom of hydrogen. Its basic properties are, however, very feeble. A metameric crystalline form, *β nitraniline* fusing at 286°, was discovered by Arppe: it is a product of the decomposition of the nitranile of pyrotartaric acid.

Hofmann represents aniline as *phenylia*, or a derivative of ammonia, in which 1 atom of hydrogen is displaced by its equivalent of a hydrocarbon $C_{12}H_5$, termed phenyl; and it is a portion of the hydrogen of the phenyl which is displaced, by chlorine, bromine, or peroxide of nitrogen, in the above-mentioned substitution-products. Neither phenyl nor its iodide have as yet been isolated; but aniline may be procured by heating hydrated carbolic (phenic) acid in a sealed tube with ammonia:—

$$\overbrace{HO,C_{12}H_5O}^{\text{Phenic acid.}} + H_3N = H_2O_2 + \overbrace{C_{12}H_5,H_2N}^{\text{Aniline.}}.$$

(1186) Several other oily bases have been discovered, homologous with aniline; they form a series, each member of which differs from the succeeding one in containing one equivalent more of the hydrocarbon (C_2H_2). The bases of this class may be obtained from a series of hydrocarbons, of the form ($C_{2n}H_{2n-6}$). These hydrocarbons when treated with nitric acid yield substitution-compounds, in which one atom of hydrogen is displaced by one of peroxide of nitrogen (NO_4); and from this nitro-compound, the corresponding base may be obtained by Zinin's process with hydrosulphate of ammonia,—4 atoms of oxygen being removed,

atoms of hydrogen are introduced into the compound
—

bon($C_{2n}H_{2n-6}$)	Nitro-substitute($C_{2n}H_{2n-7}NO_4$)		Base ($C_{2n}H_{2n-5}N$)	
. . $C_{12}H_6$	Nitrobenzol . .	$C_{12}H_5NO_4$	Aniline .	$C_{12}H_7N$
. . $C_{14}H_8$	Nitrotoluol . .	$C_{14}H_7NO_4$	Toluylia	$C_{14}H_9N$
. . $C_{16}H_{10}$	Nitroxylol . . .	$C_{16}H_9NO_4$	Xylylia .	$C_{16}H_{11}N$
. . $C_{18}H_{12}$	Nitrocumol . .	$C_{18}H_{11}NO_4$	Cuminylia	$C_{18}H_{13}N$
. . $C_{20}H_{14}$	Nitrocymol . .	$C_{20}H_{13}NO_4$	Cyminylia	$C_{20}H_{15}N$

se bases of the aniline series belong to the class of ami-
ases (1190), 1 atom of hydrogen having been displaced
hydrocarbons, $C_{12}H_5$,$C_{14}H_7$,$C_{16}H_9$, &c., but they still retain
of hydrogen in a form susceptible of displacement by
l number of equivalents of the alcohol radicles (p. 463).

b. *Pyridine Bases* $(C_{2n}H_{2n-5})'''N$.

7) A series of bases, however, exists, each member of
metameric with one of those belonging to the aniline
but in the alkaloids of this class, none of the hydrogen
of displacement by the alcohol radicles; consequently they
regarded as belonging to Hofmann's subdivision of nitrile
190). They boil at a lower temperature than the corre-
bases of the aniline series. These compounds have been
lly investigated by Anderson, and by Greville Williams.
furnished by the destructive distillation of a bituminous
m Dorsetshire; and many of them are also contained in
ucts of the distillation of bones, and of pit-coal. The
table exhibits the metameric pairs of the aniline and
groups:—

Aniline series.			Pyridine series.			
Name of base.	Boiling point. ° F.	Specific gravity of liquid.	Name of base.	Boiling point, ° F.	Specific Gravity. Liquid at 32°.	Specific Gravity. Vapour.
Unknown .			Pyridine	242	0·986	2·92
Aniline . .	360	1·080	Picoline	275	0·961	3·29
Toluylia . .	388		Lutidine	310	0·946	3·839
Xylylia . .	418		Collidine	356	0·944	
Cuminylia .	437	0·952	Parvoline			
Cyminylia .	482		Unknown			

bases of the pyridine series correspond to ammonia in
e 3 atoms of hydrogen have been displaced by 1 atom
arbon, such as $(C_{10}H_5)'''$ or $(C_{12}H_7)'''$; each of these

hydrocarbons constitutes a *triatomic group,* corresponding to three atoms of hydrogen: none of the hydrogen in these hydrocarbons admits of displacement by the alcohol radicles, but Anderson has succeeded in obtaining from the pyridine series some remarkable bases into the composition of which platinum enters. These bases have the closest connexion with those obtained by the action of ammonia on the chlorides of platinum (828). The two platinum bases from pyridine are:—

Platinopyridine = $(C_{10}H_3Pt)'''N$, or $[C_{10}H_3\ (\frac{1}{2}\,pt)_2]'''N$.
Platosopyridine = $(C_{10}H_3Pt_2)'''N$.

In the first of these compounds two atoms of hydrogen in the hydrocarbon $C_{10}H_5$, have been displaced by *one* atom of platinum, which here performs the function assigned by Gerhardt to *platinicum* (pt., eq. 49, see note to § 828); whilst in the second compound the two atoms of hydrogen are displaced by *two* atoms of platinum, the metal here discharging the function assigned to it by Gerhardt as *platinosum* (pt., eq. 98). Picoline yields similar compounds with platinum.

When the alkaloids of the pyridine group are treated with iodide of ethyl, compounds are formed belonging to the class of ammonium bases (1190). Anderson has thus obtained iodide of *ethylopyridium* $[(C_{10}H_5)'''C_4H_5N,I]$ and iodide of *ethylopicolium* $[(C_{12}H_7)'''C_4H_5N,I]$. The hydrated oxides, procured by acting upon these compounds with oxide of silver, are not volatile, and are strongly basic.

Pyridine $[(C_{10}H_5)'''N=79]$: *Sp. gr. of liquid* 0·9858; *of vapour* 2·92; *Boiling pt.* 242°.—This base is a colourless oil with a pungent smell, it is soluble in water in all proportions. It precipitates the oxides of iron, zinc, manganese, and aluminum from their salts, and forms a blue solution with the salts of copper when added in excess. Its simple salts crystallize with difficulty, but many of its double salts—particularly the double chlorides of platinum, of gold, and of copper—form well-defined crystals with facility. Pyridine may be extracted from *Dippel's oil* (a product of the destructive distillation of bones) by treating it with hydrochloric acid, and distilling the hydrochloric solution with lime. The volatile bases which come over are submitted to fractionated distillation, collecting separately those parts which come over at about 240°.

Picoline $[(C_{12}H_7)'''N=93]$: *Sp. gr. of liquid* 0·955; *of vapour* 3·29; *Boiling pt.* 275°.—This base is the one best known of the series to which it belongs. It is usually extracted from coal tar

Dippel's oil by a process similar to that employed for
collecting separately those portions of the distillate which
at about 270°. Picoline is also obtained when piperine
distilled with hydrate of potash. Picoline is a colour-
mobile, oily liquid, of a penetrating odour. It is gra-
latilized by exposure to the air, and it does not, like
ecome brown under these circumstances. By this fact,
by its lower boiling point and smaller density, picoline
distinguished from aniline. Picoline is soluble in water
portions. It is not coloured violet by chloride of lime,
affected by the addition of chromic acid to its solutions.
of picoline crystallize with difficulty, and many of
deliquescent. The hydrochlorate forms deliquescent

icoline ($C_{24}H_{14}N_2$: *Sp. gr. of liquid* 1·077).—The effect of
icoline for several hours with from $\frac{1}{8}$th to $\frac{1}{4}$th of its weight
n is remarkable. A hard, dark-brown resinous mass is
which, when freed from the excess of sodium, and
to water, is gradually decomposed. An alkaline liquid
ed containing soda and unchanged picoline, and a viscid
ured oily base collects at the bottom. If this be washed
ully distilled until the temperature rises to 380°, the
l picoline are expelled with a little carbonate of ammonia.
uing the distillation in a current of hydrogen at a tempera-
h must not be allowed to exceed 400°, and rectifying
ct a second time with similar precautions, a pale yellow
base, with a persistent characteristic empyreumatic odour,
d; it becomes brown by exposure to air. It is insoluble
but soluble in alcohol, ether, and the fixed and essential
th sulphate of copper it gives an emerald green precipi-
ble in hydrochloric acid, with which it forms a double
salts exhibit but little tendency to crystallize. The
point of interest is the fact that it is a polymeride of
presenting the closest analogy with nicotylia. Owing to
y with which it undergoes decomposition at temperatures
oiling point, it has not been practicable to ascertain the
its vapour, but there can be little doubt that the base
c, saturating 2 equivalents of an acid, and that a quantity
sented by the formula given above would yield 4 volumes
. The attempts made by Anderson to reconvert para-
nto picoline were unsuccessful. (*Edinb. Phil. Trans.*,
Both picoline and parapicoline are isomeric with aniline.

c. Quinoline Series of Bases, $(C_{2n}H_{2n-11})'''N$.

(1188) In addition to the members of the aniline and pyri series, coal tar contains a third series of bases of which quin is the most important member. Three bases of this class ar present known, viz. :—

Base.	Formula.	Boiling point. ° F.	Specific Gravity.	
			Liquid.	Vapour.
Quinoline . .	$(C_{18}H_7)'''N$	462°	1·081	4·519
Lepidine . .	$(C_{20}H_9)'''N$	510°	1·072	5·14
Cryptidine .	$(C_{22}H_{11})'''N$	525° ?		

They combine with the hydriodic ethers, and form compo corresponding to ammonium; quinoline, for instance, yields iodide of ethyl an iodide of *ethylo-quinolium* $[(C_{18}H_7)''' C_4H$ These compounds, therefore, like those of the pyridine g belong to the class of nitrile bases.

Quinoline or *Leukol* $[(C_{18}H_7)'''N = 129]$: *Sp. gr. of li* 1·081; *of vapour* 4·519; *Boiling pt.* 462°.—This alkali is re obtained by decomposing cinchonia with hydrate of potash resinous mass which is separated under the name of quino during the preparation of the salts of quinia, also yields i similar treatment. Fragments of the hydrate of potash placed in a tubulated retort, moistened with a few drops of and powdered cinchonia is added in small quantities at a time applying heat, the new base passes over, accompanied by hydrogen; if the product be redistilled, an aqueous soluti ammonia with portions of the base pass over first, and the l portions consist of nearly pure quinoline, which may be rend anhydrous by a second rectification, after it has stood for days upon chloride of calcium.

Quinoline is a colourless oil of high refracting power; it disagreeable penetrating odour, and a bitter acrid taste. mains liquid at —4°. When heated it burns with a smoky When exposed to the air it becomes slowly converted i resinous mass. If dropped upon paper it leaves a greasy which quickly disappears. It is dissolved sparingly by water it is soluble in all proportions in alcohol, ether, wood spiri bisulphide of carbon, as well as in the fixed and essentia The nitrate, the oxalate, and the bichromate of quinoline cry with facility; many double salts of quinoline, such as those wh forms with platinum, gold, palladium, and cadmium, may be ob in beautiful crystals. The platinum salt is nearly insoluble in reville Williams, by boiling 1 part of quinoline for ten es with 1½ of iodide of amyl, obtained a mass of crystals he dissolved by boiling with 6 parts of water, and then with excess of ammonia and boiled for an hour: he thus ted a resinous substance which is readily soluble in alcohol, arnishes a splendid blue dye.

ses obtained by the action of Ammonia upon Derivatives of the Alcohols.

(1189) Allusion has been already made (p. 62) to the remark- anner in which the hydrogen in ammonia may be displaced e hydrocarbons which are supposed to form the radicles of lcohols; and in consequence of this kind of substitution, com- ds are produced in which the basic character of the ammonia lly preserved, and a new series of highly interesting bodies is ed. The first bases of this description were procured by tz, who found that when the cyanic ether, or its polymeride, yanuric ether of any of the alcohols, or the corresponding (1011), was distilled with hydrate of potash, a volatile base btained homologous with ammonia, but containing the radicle he alcohol corresponding to the compound subjected to distil- n; for example:—

$$\overbrace{CH_3O.C_2NO}^{\text{hyl-cyanic ether.}} + 2(KO,HO) = \overbrace{\left.\begin{matrix}C_2H_3\\H_2\end{matrix}\right\}N}^{\text{Methylia.}} + \overbrace{2\,KO,C_2O_4}^{\text{Carb. potash.}}.$$

$$\overbrace{H_3(C_2H_3)N_2C_2O_2}^{\text{Methyl-urea.}} + 2(KO,HO) = \overbrace{\left.\begin{matrix}C_2H_3\\H_2\end{matrix}\right\}N}^{\text{Methylia.}} + H_3N + 2\,KO,C_2O_4.$$

nn (*Phil. Trans.*, 1850) found shortly afterwards that these may also be produced directly from ammonia, by acting upon lkali by means of the hydriodic or the hydrobromic ethers different alcohols. He obtained this result by enclosing, ng sealed tube, a mixture of a concentrated alcoholic solu- f ammonia, and the bromide, or the iodide derived from the l which he wished to examine. When this mixture was d for some hours in a water-bath, combination occurred, and drobromate or hydriodate of the new base was formed. , when iodide of ethyl is made to act upon a solution of am- a, the following change occurs:—

$$\overbrace{H_3N}^{\text{Ammonia.}} + \overbrace{C_4H_5I}^{\text{Iodide of ethyl.}} = \overbrace{\left.\begin{matrix}C_4H_5\\H_2\end{matrix}\right\}N,HI}^{\text{Hydriodate of ethylia.}}.$$

When the result of this reaction is distilled with hydrate of potash, ethylia is liberated, whilst water and iodide of potassium are formed. Now, if ethylia be submitted in a sealed tube to a fresh portion of iodide of ethyl, a second atom of hydrogen will be removed, and an additional equivalent of ethyl will be substituted for it, whilst the hydriodate of a new base (diethylia) is formed :—

$$\overbrace{\left.\begin{matrix}C_4H_5\\H_2\end{matrix}\right\}N}^{\text{Ethylia.}} + \overbrace{C_4H_5I}^{\text{Iodide of ethyl.}} = \overbrace{\left.\begin{matrix}(C_4H_5)_2\\H\end{matrix}\right\}N,HI}^{\text{Hydriodate of diethylia.}};$$

and if the hydriodate of diethylia be submitted to distillation with hydrate of potash, diethylia itself will be liberated. This base may in its turn be treated with a fresh portion of iodide of ethyl, and so the third atom of hydrogen may be displaced by a third equivalent of ethyl, yielding a salt which, when distilled with potash, furnishes a third base, triethylia $(C_4H_5)_3$ N.

Each of the alcohols may be made to furnish bases corresponding to each of the foregoing ethyl bases ; thus, by similar methods, a mixture of iodide of methyl and ammonia can easily be made to yield methylia, dimethylia, and trimethylia ; and from iodide of amyl, amylia, diamylia, and triamylia may be formed. These bases are all homologous with ammonia, which they closely resemble in properties. But the action of iodide of ethyl does not stop even here, for it is possible, by its means, to obtain a fourth series of bases homologous with the hypothetical body ammonium. (Hofmann, *Phil. Trans.*, 1851.) If, for example, a quantity of triethylia be heated in a tube with an additional quantity of iodide of ethyl, the two bodies enter into combination, and a compound $[(C_4H_5)_4 N,I,]$ analogous to iodide of ammonium (H_4N,I), is formed ; all the 4 atoms of hydrogen in the ammonium having been displaced by a corresponding number of equivalents of ethyl :—

$$\overbrace{(C_4H_5)_3N}^{\text{Triethylia.}} + \overbrace{C_4H_5I}^{\text{Iodide of ethyl.}} = \overbrace{(C_4H_5)_4N,I}^{\text{Iodide of tetrethylium.}}.$$

The iodide thus obtained is a crystalline substance. It is not possible to obtain the base tetrethylium, $(C_4H_5)_4$ N, in a separate form; since, like ammonium, it immediately undergoes decomposition ; but if the iodide be treated with freshly precipitated oxide of silver, double decomposition ensues, iodide of silver is formed, and the *hydrated oxide* of tetrethylium is liberated :—

$$\overbrace{(C_4H_5)_4N},I+AgO,HO = AgI+\overbrace{(C_4H_5)_4NO,HO}^{\text{Hydrated oxide of tetrethylium.}}.$$

Iodide of tetrethylium.

It might have been anticipated that, under these circumstances, oxide of tetrethylium should have been resolved into triethylia and alcohol, just as oxide of ammonium becomes broken up into ammonia and water when similarly treated: thus, since

$$H_4NI+AgO,HO \text{ yields } AgI+\left.\begin{matrix}H\\H\end{matrix}\right\}O_2+H_3N; \text{ so also}$$

$$\overbrace{(C_4H_5)_4NI}^{\text{Iodide of tetrethylium.}}+AgO,HO \text{ should become } AgI+\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}+\overbrace{(C_4H_5)_3N}^{\text{Triethylia.}};$$

but such is not the case; the new compound is very stable, and on evaporation of the solution, the hydrate of the new base may be obtained in crystals, which, like those of hydrate of potash, absorb water and carbonic acid from the atmosphere, and possess the caustic action of potash, combined with a bitter taste like that of quinia. This base forms the type of a numerous class, which are analogous to it both in composition and in properties. Hydrated oxide of tetrethylium, in common with many others like it, such as the hydrated oxide of tetramethylium [$(C_2H_3)_4NO,HO$], is sufficiently powerful to saponify the oils and to precipitate the metallic oxides from their salts, just as potash does. It forms crystallizable salts. These bases differ in a marked manner from such bases as ethylia, diethylia, and triethylia, all of which, like ammonia, are volatile without decomposition. The hydrated oxide of tetrethylium, and others which resemble it, however, cannot be volatilized without undergoing decomposition, in which case they are converted into water, a hydrocarbon homologous with olefiant gas, and a volatile alkali corresponding to triethylia; for example:—

$$\overbrace{(C_4H_5)_4NO,HO}^{\text{Hydrated oxide of tetrethylium.}}=H_2O_2+\overbrace{C_4H_4}^{\text{Olefiant gas.}}+\overbrace{(C_4H_5)_3N}^{\text{Triethylia.}}.$$

Ammonia is thus capable of originating two classes of bases, one set being volatile, and corresponding in properties to ammonia itself; the other set fixed, resembling hydrate of potash in properties, and corresponding to hydrated oxide of ammonium.

If *phenylia* ($C_{12}H_5,H_2N$), or aniline, as it is commonly termed, be employed instead of ammonia, a corresponding series of bases may be obtained from it, in which the two atoms of hydrogen may be successively displaced by one equivalent of one of the alcohol radicles; and finally, the compound may be converted into an ammonium base by the action of another atom of iodide of ethyl; thus aniline (or phenylia) $\left.\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right\}N$, becomes, when treated with iodide of ethyl, successively, 1. ethyl-phenylia $\left.\begin{matrix}C_{12}H_5\\C_4\,H_5\\H\end{matrix}\right\}N$; 2. diethyl-phenylia $\left.\begin{matrix}C_{12}H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}N$; 3. and finally, hydrated oxide of triethyl-phenylium $\left.\begin{matrix}C_{12}H_5\\C_4\,H_5\\C_4\,H_5\\C_4\,H_5\end{matrix}\right\}NO,HO.$

Hofmann, in the further investigation of this remarkable method of preparing artificial bases, found that each of the three atoms of hydrogen in ammonia may be displaced by a different alcohol radicle. Thus it is possible to obtain, first, methylia, by the action of iodide of methyl upon ammonia; then by acting upon methylia with iodide of ethyl, the compound methyl-ethylia (corresponding to diethylia) is formed:—

$$\left.\begin{matrix}C_2H_3\\H\\H\end{matrix}\right\}N+\overbrace{C_4H_5I}^{\text{Iodide of ethyl.}}=\left.\begin{matrix}C_2H_3\\C_4H_5\\H\end{matrix}\right\}N,HI;$$

and on distilling this hydriodate of methyl-ethylia with hydrate of potash, the new base is liberated. Now, if methyl-ethylia be treated with iodide of amyl, a compound corresponding to triethylia is formed, but containing, in the place of the three equivalents of ethyl, 3 different alcohol radicles, thus:—

$$\overbrace{\left.\begin{matrix}C_2H_3\\C_4H_5\\H\end{matrix}\right\}N,HI}^{\text{Hydriodate of methyl-ethylia.}}+\overbrace{C_{10}H_{11}I}^{\text{Iodide of amyl.}}=\overbrace{\left.\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_{10}H_{11}\end{matrix}\right\}N,HI.}^{\text{Hydriodate of methyl-ethyl-amylia.}}$$

Hofmann even succeeded in obtaining an ammonium base, derived from aniline, containing 4 different hydrocarbon radicles, and to which the unwieldy name of hydrated oxide of methyl-ethyl-amylo-phenylium must be assigned:—

$$\left.\begin{matrix}C_2\,H_3\\C_4\,H_5\\C_{10}H_{11}\\C_{12}H_5\end{matrix}\right\}\begin{matrix}=\quad C_{28}H_{24}NO,HO;\text{ or}\\NO,HO=\left.\begin{matrix}C_2H_3,C_4H_5,C_{10}H_{11},C_{12}H_5.N\\H\end{matrix}\right\}O_2.\end{matrix}$$

It, of course, will not be overlooked that if the ordinary salts of ammonia are supposed to be compounds of ammonium, the salts of all the bases derived from ammonia ought to be considered from the same point of view :—If hydriodate of ammonia be regarded as iodide of ammonium, hydriodate of ethylia should be iodide of ethylium, and the composition and nomenclature of the ethyl bases would be simply translated thus; no hydriodates of the ammonium bases are known :—

$$\overbrace{(C_4H_5)\,H_2N,HI}^{\text{Hydriodate of ethylia.}} = \overbrace{(C_4H_5)\,H_3N,I}^{\text{Iodide of ethylium.}};$$

$$\overbrace{(C_4H_5)_2HN,HI}^{\text{Hydriodate of diethylia.}} = \overbrace{(C_4H_5)_2H_2N,I}^{\text{Iodide of diethylium.}};$$

$$\overbrace{(C_4H_5)_3\quad N,HI}^{\text{Hydriodate of triethylia.}} = \overbrace{(C_4H_5)_3H\,N,I}^{\text{Iodide of triethylium.}};$$

$$\overbrace{\text{wanting.}}^{\text{Hydriodate of oxide of tetrethylium.}} \qquad \overbrace{(C_4H_5)_4\quad N,I.}^{\text{Iodide of tetrethylium.}}$$

In this work, however, for the sake of marking the distinction between the volatile and the fixed bases, the termination *ium* will be reserved for such bases as are formed upon the type of hydrated oxide of ammonium.

An important circumstance, in relation to the molecular constitution of ammonia, was elicited in the course of these investigations. Let the three atoms of hydrogen in ammonia be represented by the letters *h*, H and *H;* and let $\left.\begin{matrix}h\\ \mathrm{H}\\ H\end{matrix}\right\}\mathrm{N}$ = ammonia:—it might be supposed that the three different atoms of hydrogen *h*, H, and *H*, in the molecule of ammonia, might each have a different function to perform in the alkaline group. Suppose, then, that a derivative base were formed, in which the atom of hydrogen *h* were replaced by a radicle called X, forming a new base $\left.\begin{matrix}\mathrm{X}\\ \mathrm{H}\\ H\end{matrix}\right\}\mathrm{N}$; the other atoms of hydrogen, H and *H*, admit of being displaced respectively by other radicles, Y and Z. Suppose, for example, that X represents phenyl ($C_{12}H_5$), Y, amyl, and Z, ethyl; the question is, whether the same compound will be formed indifferently when amyl is substituted for H, and ethyl for *H*, or when ethyl supplies the place of H, and amyl of *H*. Whether in fact, there will be any perceptible difference if the compound be obtained in the form of $\left.\begin{matrix}\mathrm{X}\\ \mathrm{Y}\\ \mathrm{Z}\end{matrix}\right\}\mathrm{N}$; or of $\left.\begin{matrix}\mathrm{X}\\ \mathrm{Z}\\ \mathrm{Y}\end{matrix}\right\}\mathrm{N}$. To decide this point Hofmann carefully compared the properties of phenyl-ethyl-amylia

($C_{26}H_{21}N$), prepared by acting upon phenyl-amylia $\left.\begin{matrix}C_{12}H_5\\C_{10}H_{11}\\H\end{matrix}\right\}N$, bromide of ethyl ($C_4H_5Br$), which would yield $\left.\begin{matrix}C_{12}H_5\\C_{10}H_{11}\\C_4\,H_5\end{matrix}\right\}N$, with the compound phenyl-ethyl-amylia $\left.\begin{matrix}C_{12}H_5\\C_4\,H_5\\C_{10}H_{11}\end{matrix}\right\}N$, formed by decomposing phenyl-ethylia $\left.\begin{matrix}C_{12}H_5\\C_4\,H_5\\H\end{matrix}\right\}N$, with bromide of amyl ($C_{10}H_{11}Br$); but the two substances comported themselves alike in all respects. The two bodies thus obtained are, therefore, not only isomeric, but identical, and the functions of the two atoms of hydrogen H and *H* in ammonia must be similar. The case, however, is very different if alkalies be compared together which have the same empirical formulæ, but which have been produced by the substitution of dissimilar alcohol radicles.

In order to render this evident, we may take for example the bases of the aniline series (1186).

Toluylia has the same composition as the methyl-phenylia; xylylia as ethyl-phenylia, and cuminylia as methyl-ethyl-phenylia. These pairs of substances are, however, only metameric, they are not identical. Toluylia is a fusible crystalline solid, which boils at 388°, and yields stable, sparingly soluble salts with most of the acids, including a beautiful crystallizable double salt with bichloride of platinum. Methyl-phenylia is an oily liquid which boils at 377°; its platinum salt is of a pale yellow colour, and begins to blacken almost immediately after its formation: all its salts are distinguished by their solubility, and the facility with which they are decomposed,—aniline being reproduced; whilst toluylia does not yield aniline under any known circumstances. The properties of cuminylia and methyl-ethyl-phenylia, though both are liquid at ordinary temperatures, are not less distinct.

Further, it is possible to introduce an equivalent of ethyl into toluylia; one of the atoms of hydrogen which this base contains being readily eliminated when the alkali is treated with iodide of ethyl. The ethylo-toluylia thus obtained is a third alkali isomeric or metameric with cuminylia, yet possessed of properties quite distinct from it. Hence it is evident that three different bases are *already* known, all of which possess the empirical formula $C_{18}H_{13}N$; *and there* is no doubt that besides these, three other bases, each having the same empirical formula and the same combining equivalent, could readily be obtained; yet each of these new bases would differ in constitution from the foregoing bases and from each other: they would also probably be found to differ in properties. The first of these new bases (methylo-xylylia) might be formed by substituting an atom of methyl for 1 of hydrogen in xylylia; the second (dimethylo-toluylia would be formed by substituting 2 equivalents of methyl in toluylia for 2 atoms of hydrogen; the third, trityl-phenylia, would be obtained by substituting trityl (C_6H_7), the radicle of tritylic alcohol (C_6H_7O,HO), for one of the atoms of hydrogen in aniline. The six bases metameric with cuminylia would therefore have the composition which is represented in the following table:—

Known bases.	*Bases not yet formed.*
Cuminylia. $\left.\begin{matrix}\overbrace{C_{18}H_{11}}\\ H\\ H\end{matrix}\right\}N$	Methylo-xylylia. $\left.\begin{matrix}\overbrace{C_{16}H_{9}}\\ C_{2}H_{3}\\ H\end{matrix}\right\}N$
Ethylo-toluylia. $\left.\begin{matrix}\overbrace{C_{14}H_{7}}\\ C_{4}H_{5}\\ H\end{matrix}\right\}N$	Dimethylo-toluylia. $\left.\begin{matrix}\overbrace{C_{14}H_{7}}\\ C_{2}H_{3}\\ C_{2}H_{3}\end{matrix}\right\}N$
Methyl-ethyl-phenylia. $\left.\begin{matrix}\overbrace{C_{12}H_{5}}\\ C_{4}H_{5}\\ C_{2}H_{3}\end{matrix}\right\}N$	Trityl-phenylia. $\left.\begin{matrix}\overbrace{C_{12}H_{5}}\\ C_{6}H_{7}\\ H\end{matrix}\right\}N$

The manner in which toluylia and other bases not derived from the alcohols admit of being attacked by the hydriodic and hydrobromic ethers shows that the action of these ethers upon the different bases affords a most important means of examining and dissecting these various compounds; and it has been found to be applicable to organic bases both of natural and artificial origin. Within the few years that have elapsed since Hofmann first showed the applicability of these reagents to this purpose, extensive use has been made of them in such examinations.

(1190) *Hofmann's Classification of Organic Bases.*—Hofmann originally proposed to classify the various monatomic bases which may be produced by these methods of substitution, under the heads of *amidogen*, *imidogen*, *nitrile* and *ammonium* bases—a distinction still useful, although he has since termed the amidogen bases *primary monamines*, the imidogen bases *secondary monamines*, and the nitrile bases *tertiary monamines*. The bases, in fact, differ from the amides in the fact that they contain the basic radicles of the alcohols, whilst the corresponding amides (1170 *et seq.*) contain the acid radicles in the *place of the* hydrogen of the original mole-

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	Ethylia . (C_4H_7N) $\left.\begin{matrix}C_4H_5\\H\\H\end{matrix}\right\}N$	Diethylia . . ($C_8H_{11}N$) $\left.\begin{matrix}C_4H_5\\C_4H_5\\H\end{matrix}\right\}N$	Triethylia ($C_{12}H_{15}N$) $\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N$	Hydrated oxide of tetrethylium ($C_{16}H_{20}NO,HO$) $\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}NO,HO$
	Amylia . ($C_{10}H_{12}N$) $\left.\begin{matrix}C_{10}H_{11}\\H\\H\end{matrix}\right\}N$	Diamylia . . ($C_{20}H_{22}N$) $\left.\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\H\end{matrix}\right\}N$	Triamylia . . ($C_{30}H_{33}N$) $\left.\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right\}N$	Hydrated oxide of tetramylium ($C_{40}H_{44}NO,HO$) $\left.\begin{matrix}C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\\C_{10}H_{11}\end{matrix}\right\}NO,HO$
	Aniline . (Phenylia $C_{12}H_7N$) $\left.\begin{matrix}C_{12}H_5\\H\\H\end{matrix}\right\}N$	Ethylphenylia, or ethylaniline ($C_{16}H_{11}N$) $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\H\end{matrix}\right\}N$	Diethylphenylia, or Diethylaniline . ($C_{20}H_{15}N$) $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N$	Hydrated oxide of triethylophenylium ($C_{24}H_{20}NO,HO$) $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}NO,HO$
Phosphuretted Hydrogen (H_3P) $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}P$		Methylphenylia, or methylaniline ($C_{14}H_9N$) $\left.\begin{matrix}C_{12}H_5\\C_2H_3\\H\end{matrix}\right\}N$	Methyl-ethyl-phenylia, or methyl-ethyl-aniline ($C_{18}H_{13}N$) $\left.\begin{matrix}C_{12}H_5\\C_4H_5\\C_2H_3\end{matrix}\right\}N$	Hydrated oxide of methyl-ethyl-amylophenylium ($C_{28}H_{24}NO,HO$) $\left.\begin{matrix}C_{12}H_5\\C_{10}H_{11}\\C_4H_5\\C_2H_3\end{matrix}\right\}NO,HO$
Arseniuretted Hydrogen (H_3As) $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}As$			Methyl-ethyl amylia . . . ($C_{16}H_{19}N$] $\left.\begin{matrix}C_{10}H_{11}\\C_4H_5\\C_2H_3\end{matrix}\right\}N$	Hydrated oxide of methyl-diethyl-amylium ($C_{20}H_{24}NO,HO$) $\left.\begin{matrix}C_{10}H_{11}\\C_4H_5\\C_4H_5\\C_2H_3\end{matrix}\right\}NO,HO$
	Chlorophenylia, or chloraniline ($C_{12}H_6ClN$) $\left.\begin{matrix}C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\\H\\H\end{matrix}\right\}N$	Ethylochlorophenylia, or ethylochloraniline ($C_{16}H_{10}ClN$) $\left.\begin{matrix}C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\\C_4\ H_5\\H\end{matrix}\right\}N$	Diethylochlorophenylia, or diethylochloraniline ($C_{20}H_{14}ClN$] $\left.\begin{matrix}C_{12}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.\\C_4\ H_5\\C_4\ H_5\end{matrix}\right\}N$	
Antimoniuretted H	Toluylia . $\left.\begin{matrix}C_{14}H_7\\H\end{matrix}\right\}N$	Ethylotoluylia $\left.\begin{matrix}C_{14}H_7\\C_4H_5\end{matrix}\right\}N$	Dimethylotoluylia $\left.\begin{matrix}C_{14}H_7\\C_2H_3\\C_2H_3\end{matrix}\right\}N$	

of ammonia. Amidogen bases are those which may be
ded as still retaining two atoms of the hydrogen of the original
onia, one atom only of hydrogen having been displaced by a
carbon. In the imidogen bases the substitution has pro-
ed a step further; one atom of hydrogen of the original ammonia
being left; whilst in the nitrile bases none of the hydrogen of
mmonia remains. In the ammonium bases a fourth equivalent
hydrocarbon is superadded, and takes the place of the fourth
of hydrogen theoretically assigned to ammonium. All the
nium bases while separated from their salts contain at least one
alent of water, and they are therefore only known in the form
drates. The table on the preceding page will afford an illustra-
f the mode of classifying the different bases upon this principle.
here can be no doubt that in certain cases the vegetable
es as they exist in the plant, are formed upon the type
monia; though in the present state of our knowledge upon
ubject we are far from warranted in drawing the general con-
n that such is their constitution in all instances. The two
last mentioned in the table, viz., conylia and nicotylia, are
tural volatile alkalies contained respectively in hemlock and
acco. On treating conylia with iodide of methyl, two com-
s were formed, the simpler of which may be considered as a
e base, and the more complicated one as an ammonium base;
a itself being regarded as an imidogen base in which the
ic group $(C_{16}H_{14})''$ has displaced 2 atoms of hydrogen,
nicotylia must be regarded as a diatomic nitrile base, formed
the type of 2 molecules of ammonia, in which the 3 atoms
drogen in each atom of ammonia have been displaced by the
ic group $(C_{10}H_7)'''$.

1191) **Methylia**; *methylamine* $(C_2H_5N = C_2H_3,H_2N = 31)$: *Sp.*
vapour 1·08.—This body is gaseous under ordinary circum-
es, but may be condensed by a freezing mixture to a very
le liquid, which is not solidified by exposure to a bath of solid
ic acid and ether. It is colourless, and has an intensely
ent odour of ammonia, and an extremely powerful alkaline
on, producing dense white fumes when exposed to the vapour
drochloric acid; but it is distinguished from ammonia by its
lammability; it burns with a yellowish livid flame, and
arbonic acid, water, and nitrogen, accompanied, if the
ir be insufficient, with traces of cyanogen or of hydro-
Methylia is more soluble in water than any other
at 55° water dissolves 1150 times its bulk, forming a

cinic
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is nea
water
solve i
Su
H_2N_2-
consist
evapor
It may
succini
consid

[illegible]	Aniline (phenylia) [illegible]	Methylphenylia, or methylaniline [illegible]	Methyl ethyl amylia [illegible]	Hydrated oxide of [illegible] NO,HO
[illegible]	[illegible]	Ethylphenylia, or ethylaniline [illegible]	Diethylphenylia, or diethylaniline [illegible]	Hydrated oxide of methyl-ethyl-amylphenylium [illegible] NO,HO
[illegible]	[illegible]	[illegible]	Methyl-ethyl-phenylia, or methyl-ethyl-aniline [illegible]	Hydrated oxide of methyl-ethyl-amylium [illegible] NO,HO
[illegible]	[illegible]	[illegible]	Diethylochlorophenylia, or diethylochloraniline [illegible]	[illegible]

ammonia. Amidogen bases are those which may be
d as still retaining two atoms of the hydrogen of the original
ia, one atom only of hydrogen having been displaced by a
rbon. In the imidogen bases the substitution has pro-
a step further; one atom of hydrogen of the original ammonia
ing left; whilst in the nitrile bases none of the hydrogen of
monia remains. In the ammonium bases a fourth equivalent
drocarbon is superadded, and takes the place of the fourth
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type of 2 molecules of ammonia, in which the 3 atoms
en in each atom of ammonia have been displaced by the
group $(C_{10}H_7)'''$.

METHYLIA; *methylamine* $(C_2H_5N = C_2H_3, H_2N = 31)$: *Sp.*
our 1·08.—This body is gaseous under ordinary circum-
it may be condensed by a freezing mixture to a very
uid, which is not solidified by exposure to a bath of solid
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dour of ammonia, and an extremely powerful alkaline
roducing dense white fumes when exposed to the vapour
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mmability; it burns with a yellowish livid flame, and
carbonic acid, water, and nitrogen, accompanied, if the
air be insufficient, with traces of cyanogen or of hydro-
Methylia is more soluble in water than any other
55° water dissolves 1150 times its bulk, forming a

powerfully alkaline solution with a very pungent ammoni odour, and a strongly caustic action upon the skin; when b the alkali is expelled in the gaseous form. Solution of meth acts upon solutions of the metallic salts, as ammonia woul dissolving the precipitated oxides of zinc, silver, and copper, the latter case forming a deep blue liquid. The oxides of mium, of cobalt, and of nickel, are precipitated by methylia, are not redissolved by it.

When methylia is passed through a porcelain tube heat redness, it is decomposed; hydrocyanate of ammonia, and a g mixture of hydrocyanic acid, hydride of methyl, and free hydr being formed :—

$$3\,\overbrace{C_2H_5N}^{\text{Methylia.}} = \overbrace{H_3N,HC_2N}^{\text{Hydrocy. ammon.}} + HC_2N + \overbrace{C_2H_3,H}^{\text{Hydride of methyl.}} + 3\,H_2.$$

If potassium be heated in gaseous methylia, cyanide of p sium is formed, and hydrogen is liberated; $2\,C_2H_5N + K_2 =$ $C_2N) + 5\,H_2$.

Preparation.—Methylia is readily obtained by disti carefully dried hydrochlorate of the base with twice its we quicklime. The operation should be performed in a long the lower half of which is filled with the mixture, and the half with hydrate of potash, in order to dry the gas compl it may be collected in jars over mercury. Hydrochlor methylia is best obtained for this purpose by distilling cya of methyl with hydrate of potash (1012), and saturating the tillate with hydrochloric acid; the residue when evaporat dryness may be dissolved in boiling absolute alcohol, from on cooling it crystallizes in large iridescent foliated delique crystals: at a temperature a little above 212° it fuses, and heated in an open vessel it volatilizes in dense white clouds, may be condensed unchanged. This salt does not yield amalgam similar to that of ammonium when decomposed b voltaic battery in contact with mercury, nor when its concen solution is mixed with an amalgam of potassium.

Methylia is likewise a frequent product of the destructiv tillation of azotised substances; it is also present amongst bases when many natural alkaloids—such as narcotine, m codeia, and caffeine—are distilled with caustic potash.

Most of the salts of methylia are very soluble in water; hydrochlorate forms with bichloride of platinum a soluble pound, crystallizing in golden yellow scales, which are insol alcohol.

nethylia ($C_6H_9N=3\ C_2H_3,N$).—This alkali, which is iso-ith tritylia (C_6H_7, H_2N), is found in considerable quantity roe of herrings. It has an extremely powerful and dis-le fishy odour. It is also obtained by distilling ergot of rye drate of potash; and it imparts to the *Chenopodium vulva-* peculiar odour. Trimethylia is a very volatile liquid, which about 41°, and emits an inflammable vapour very soluble r. Iodide of methyl immediately converts this base into a of crystals of iodide of tetramethylium.

ramethylium.—The iodide of this base is the principal pro-rmed by heating iodide of methyl in excess with a solution nonia in wood spirit or in alcohol. Since the iodide of ethylium is sparingly soluble in cold water, it may be puri-m the accompanying hydriodates of methylia, dimethylia, imethylia, by crystallization from boiling water. When with recently precipitated oxide of silver, iodide of silver ed, and a hydrated oxide of tetramethylium [($C_2H_3)_4NO$, emains in solution; it may be obtained by evaporation *in* over sulphuric acid, in crystals which are deliquescent, and carbonic acid. Its salts crystallize well, particularly the , which forms long brilliant needles. The double chloride inum and tetramethylium ($C_8H_{12}NCl,PtCl_2$), crystallizes in ficent dark orange-coloured octohedra.

hen the hydrated oxide of tetramethylium is treated with an nal quantity of iodide of methyl, no further combination of l with the base occurs; but double decomposition ensues, of tetramethylium is formed, and wood spirit is libe-

—

$$\overbrace{(C_2H_3)_4NO,HO}^{\text{Oxide of tetramethylium.}}+\overbrace{C_2H_3,I}^{\text{Iodide of methyl.}}=\overbrace{C_2H_3O,HO}^{\text{Wood spirit.}}+\overbrace{(C_2H_3)_4N,I.}^{\text{Iodide of tetramethylium.}}$$

92) Ethylia, or *Ethylamine* ($C_4H_7N=C_4H_5,H_2N=45$): *Sp. liquid* 0·696; *of vapour* 1·594; *Boiling pt.* 65°·6.—This base tutes a volatile, mobile colourless liquid, which emits an inflam-vapour of a pungent ammoniacal odour. It is miscible ater in all proportions, but, by prolonged boiling, the whole ethylia may be expelled. Ethylia produces results with ns of metallic salts very similar to those of methylia, from , however, it may be distinguished by the power possessed ylia of dissolving recently precipitated alumina. Wurtz has ed to take advantage of this property as a means of sepa-alumina from oxide of iron, in the operations of analysis. a displaces ammonia from its salts if evaporated with

them. It yields dense white fumes with vapours of hydrochloric acid.

Ethylia may be prepared in a manner similar to that directed for methylia, by acting upon cyanic or cyanuric ether with hydrate of potash. It may also be obtained by acting upon iodide of ethyl with ammonia, in which case hydriodate of ethylia is formed; the salts of ethylia do not generally crystallize with facility; they are soluble in water and in alcohol. The hydrochlorate forms colourless plates, which are fusible at 169°. The sulphate is deliquescent, and since it is soluble in alcohol it may readily be separated from sulphate of ammonia, which is insoluble in this menstruum. The double salt with bichloride of platinum ($C_4H_7N,HCl,PtCl_2$), crystallizes in yellow octohedra.

Diethylia [$C_8H_{11}N=(C_4H_5)_2HN$; *Boiling pt.* 134°·6] is a colourless, volatile, inflammable liquid, powerfully alkaline, and very caustic. It may be obtained by treating ethylia with iodide of ethyl in the manner already described (1189).

Triethylia [$C_{12}H_{15}N=(C_4H_5)_3N$; *Boiling pt.* 196°] is also a soluble, volatile, and powerful base, which forms a beautiful orange double salt with bichloride of platinum, crystallizing in large rhombic tables [$(C_4H_5)_3N,HCl,PtCl_2$]. Triethylia may be obtained from the foregoing base by the action of iodide of ethyl upon it. The salts of tetrethylium are procured by continuing the action of iodide of ethyl upon triethylia.

The *hydrated oxide of tetrethylium* is a powerful base, perfectly analogous to the corresponding compound of tetramethylium. It may be obtained in solution by treating the iodide of tetrethylium with oxide of silver. If this solution be allowed to evaporate *in vacuo* over sulphuric acid, the base forms long hair-like needles, which are very deliquescent, and absorb carbonic acid with great avidity. A strong solution of the base may be boiled without undergoing decomposition, but if evaporated to dryness over the water-bath, it becomes decomposed as soon as the water is nearly all expelled. A solution of the base acts powerfully upon the cuticle, and it saponifies the fats as readily as potash, forming soft soaps. The oxide of tetrethylium is not liberated from its iodide by the action of potash; on adding a solution of potash to one of the iodide of the base, a crystalline mass of the pure iodide of tetrethylium is separated, as it is less soluble in alkaline liquids than in pure water: even when boiled with the concentrated solution of potash for some hours, no decomposition is effected; but it is decomposed with facility by the salts of silver, or by the freshly precipitated oxide of silver. Analogous reactions with potash and oxide of are found to occur with a large number of other ammonium . The iodides of the ammonium bases combine with an onal quantity of iodine and form crystallizable compounds may be obtained by mixing a solution of iodine in alcohol he alcoholic solution of the iodide of the base. The *teriodide rethylium* $(C_4H_5)_4N,I_3$ crystallizes in dark violet brilliant . The *pentiodide* $(C_4H_5)_4N,I_5$ forms tabular plates of a bril- etallic lustre and a dark greenish grey colour.

Bases derived from other Alcohols.

93) *Tritylia* or *propylamine* (C_6H_7,H_2N) is isomeric with ylia; it is one of the bases obtained by Anderson during structive distillation of bones; and the same chemist has e procured from Dippel's oil another base, which he termed e, but which corresponds to *tetrylia* or *butyria* (C_8H_9,H_2N), ali of tetrylic alcohol; it also occurs mixed with amylia in tillate when wool or flannel is distilled with hydrate of potash. bases are liquid and volatile.

series of bases corresponding to those from methylic and alcohols has also been obtained from fousel oil. Their owers are smaller than those of the ethyl and methyl series, ey present no particular points of interest. *Amylia* $(C_{10}H_{11}$ is a very light, colourless, inflammable liquid, which boils

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ofmann finds that the mixed ethylic bases may be completely and eparated when in their anhydrous form, by treating them with her. Ethylia is thus converted into a beautiful sparingly soluble lisable compound, *diethyloxamide;* diethylia furnishes *ethyloxamic ether*, liquid which boils at a high temperature; and triethylia remains unal-

$$\overbrace{\left.\begin{matrix}O_4)''\\ H_5)_2\end{matrix}\right\}O_4}^{\text{ether.}}+2\Bigg(\overbrace{\left.\begin{matrix}C_4H_5\\H_2\end{matrix}\right\}N}^{\text{Ethylia.}}\Bigg)=\overbrace{\left.\begin{matrix}(C_4O_4)''\\(C_4H_5)_2\\H_2\end{matrix}\right\}N_2}^{\text{Diethyloxamide.}}+2\Bigg(\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}\Bigg);$$

$$\overbrace{\left.\begin{matrix}O_4)''\\ H_5)_2\end{matrix}\right\}O_4}^{\text{ether.}}+\overbrace{\left.\begin{matrix}(C_4H_5)_2\\H\end{matrix}\right\}N}^{\text{Diethylia.}}=\overbrace{\left.\begin{matrix}(C_4O_4)''(C_4H_5)_2N\\C_4H_5\end{matrix}\right\}O_2}^{\text{Diethyloxamic ether.}}+\overbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}^{\text{Alcohol.}}.$$

distilling the result of the reaction of oxalic ether on the mixed bases, triethylia passes over pure. The crystals of diethyloxamide ed by crystallization from boiling water, and when decomposed by yield pure ethylia. The oily diethyloxamic ether when cooled to 32° s a few crystals of diethyloxamide; if decanted from these and dis- ed the portions collected which come over at 500°, the product is pure amic ether; and this when distilled with hydrate of potash furnishes thylia. Mr. Lea takes advantage of the difference in the solubility rbazotates of these bases to effect their separation.

at 203°, and is of sp. gr. 0·750. It is soluble in water in all proportions. Horn when distilled with hydrate of potash was found by Limpricht to yield 4 or 5 per cent. of this base. Its salts crystallize readily.

The alcohol from castor oil (octylic alcohol) also yields a well-marked base, *octylia* or *caprylia* ($C_{16}H_{17},H_2N$); and even the alcohol of palmitic acid, ethal, has been made to yield a compound ammonia in which all the three equivalents of hydrogen have given place to the hydrocarbon of cetyl, thus forming *tricetylia* $(C_{32}H_{33})_3N$, which crystallizes in white fusible needles, freely soluble in boiling alcohol. Its salts are not soluble in water, but they crystallize readily from boiling alcohol and from ether.

3. *Alcohol Bases obtained from phosphuretted, arseniuretted, and antimoniuretted hydrogen.*

(1194) The first column of the table of bases given (p. 464) includes three substances which do not possess basic properties, but which present the closest analogy in composition with ammonia; viz., phosphuretted, arseniuretted, and antimoniuretted hydrogen. Each of them contains three atoms of hydrogen, and one atom of their characteristic components; and they may be looked upon as analogues, or representatives of ammonia, in which the nitrogen has been displaced respectively by phosphorus, arsenic, and antimony. Widely as these three elements differ from nitrogen in their separate form, they yet exhibit a considerable analogy with it in their mode of entering into combination; all three of them forming not only corresponding compounds with three atoms of hydrogen, but, like nitrogen, all of them yielding with oxygen powerful acids which contain five atoms of oxygen.

Neither arseniuretted nor antimoniuretted hydrogen exhibits any basic properties, and the only indication of basic power in the case of phosphuretted hydrogen consists in the formation of volatile crystalline bodies with hydrobromic and hydriodic acids (376); yet it has been shown by P. Thénard, that if the hydrogen of phosphuretted hydrogen be displaced by methyl or by ethyl, powerful bases may be procured, formed upon the type of ammonia, but containing phosphorus instead of nitrogen, and ethyl or methyl in the place of hydrogen. Hofmann and Cahours have investigated these compounds more minutely (*Phil. Trans.* 1857), and have described a method by which they may be obtained with certainty. The process introduced by the chemists last named, for the preparation of these phosphorised bases consists in mixing terchloride of phosphorus (PCl_3) with zinc-methyl, zinc-ethyl, &c., when chloride of zinc is formed, whilst the new base is produced. Many of these bases have a most offensive odour, and the vapour of several of them when mixed with atmospheric air, or with oxygen, takes fire, especially if the temperature be slightly raised. But not only may phosphorised bases $(C_2H_3)_3P$; $(C_4H_5)P_3$; $(C_{10}H_{11})_3P$, &c., analogous to ammonia, be formed, but by treating these new bases with iodide of ethyl, of methyl, or of amyl, iodides of ammonium-bases analogous to that of tetrethylium may be obtained; and by the action of oxide of silver upon these iodides, hydrates of the new ammonium-bases may be procured.

(1195) *Phosphotriethylia*, or *triethylphosphine* $[(C_4H_5)_3P=118]$. *Sp. gr. of liquid* 0·812; *Boiling pt.* 261°.—This interesting compound is a colourless, transparent liquid of high refracting power, insoluble in water, but freely soluble in alcohol and in ether. It has a benumbing odour, which, when largely diluted, greatly resembles that of hyacinths. The reaction by which it is formed may be represented by the following equation :—

$$2\,PCl_3+3\,\overbrace{[(C_4H_5)_2Zn_2]}^{\text{Zinc ethyl.}}=6\,ZnCl+\overbrace{2\,[(C_4H_5)_3P]}^{\text{Phosphotriethylia.}}$$

In order to prepare phosphotriethylia the arrangement of apparatus represented in the annexed figure (Fig. 364) was adopted :—

a is a gas-bottle for generating carbonic acid; *b* a wash-bottle containing sulphuric acid; *c* a reservoir of carbonic acid; *d* a bent tube containing terchloride of phosphorus; *e* a receiver; *f* a retort containing a solution of zinc-ethyl in ether; *g* a reservoir for terchloride of phosphorus; the supply being regulated by a glass stop-cock. The whole apparatus is first filled with dry carbonic acid gas. The tube in *c*, which at first was closed with

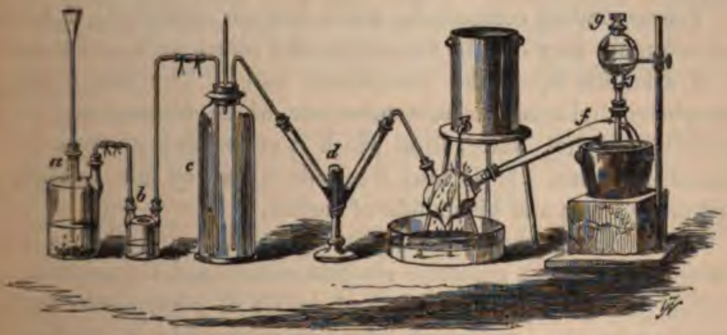

FIG. 364.

a cap of caoutchouc, is opened, and the ethereal solution of zinc-ethyl is distilled into the retort, after which the globe with the terchloride of phosphorus is fixed in its place; the terchloride is allowed to enter drop by drop, whilst the retort is cooled by immersion in ice-cold water. The action is very violent. As soon as heat is no longer evolved by addition of terchloride of phosphorus the decomposition is completed.

In the retort and the receiver are two layers of liquid, one a pale, heavy, straw-coloured viscid liquid, the compound of phosphotriethylia and chloride of zinc; the other a colourless mobile fluid, which is a solution of terchloride of phosphorus in ether, and which may be poured off and used in a subsequent similar operation. In order to separate the phosphorus base, the compound is decomposed by means of potash. For this purpose the mass in the retort is first diluted with water, then the retort is filled with hydrogen and a concentrated solution of potash allowed to flow slowly into it. On subsequently distilling, in a very slow stream of hydrogen, phosphotriethylia passes over with the aqueous vapour, and forms a layer which floats on the top of the condensed water in the receiver.

Phosphotriethylia, by slow oxidation, is converted into a crystalline, volatile, very deliquescent mass, of the formula $[(C_4H_5)_3P,O_2]$; (*Fusing pt.* 111°·2; *Boiling pt.* 464°; *Sp. gr. of vapour* 4·60): it corresponds to the binoxide of stibiotriethyl (1035).

Corresponding compounds, which contain sulphur $(C_4H_5)_3P,S_2$, and selenium may also be formed by the direct action of sulphur or of selenium upon the phosphorus base. The *bisulphide* of phosphotriethylia is a volatile substance which fuses at 201°. It it soluble in hot water, from which it crystallizes in remarkably beautiful needles. It is also freely dissolved by hot alcohol, as well as by ether and bisulphide of carbon.

On treating phosphotriethylia with iodide of ethyl, a very powerful and almost explosive reaction occurs, and the mixture, on cooling, yields a crystalline mass of iodide of *phosphotetrethylium* (tetrethylphosphonium) which, when decomposed by oxide of silver, yields a strongly alkaline solution of the hydrated oxide of the base $[(C_4H_5)_4PO,HO]$; it has a bitter phosphoric taste, and yields crystallizable deliquescent salts. When this hydrated base is heated, it gives off a compound of carbon and hydrogen, and at a higher temperature furnishes crystals of the binoxide of phosphotriethylia $(C_4H_5)_3P,O_2$.

Both arsenic and antimony form with ethyl and methyl, and the other alcohol radicles, compounds which combine with oxygen, and possess basic properties as powerful as those of many of the metallic oxides (1030, 1035).

4. *Polyatomic Bases.*

(1196) Recent researches, especially those of Hofmann, have shown that, in addition to the monatomic bases, or bases formed upon the type of a single atom of ammonia, others may be obtained, which are produced by substitution from two, from three, or even from a still larger number of atoms of ammonia. So that we have diatomic and triatomic bases, or diammonias and triammonias formed from the diatomic and triatomic alcohols, just as the monammonias are from the monatomic alcohols.

When, for instance, bibromide of ethylene is decomposed by ammonia, a complex reaction occurs; but among the products two substances are always present as hydrobromates, viz., ethylene-diammonia, or *ethylenia*, and diethylene-diammonia, or *diethylenia*.* Each of these bases is formed from two atoms of ammonia, and requires two equivalents of a monobasic acid for its saturation. This formation may be illustrated by the subjoined equations:†—

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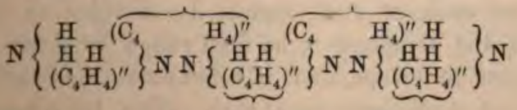
* In studying these compounds on the type of diammonium, Hofmann found it far more advantageous to use phospho-triethylia than ammonia as the compound from which they were formed. The number of compounds obtainable from phospho-triethylia by substitution is much smaller than that obtainable from ammonia, inasmuch as the three displaceable atoms of hydrogen which ammonia contains have been already displaced in the phosphorus base.

When ammonia is acted upon by means of bibromide of ethylene, compounds may be obtained in which the hydrogen may be successively displaced by the diatomic radicle $(C_4H_4)''$, and by the monatomic radicles $(C_4H_3)'$ $(C_4H_4Br)'$ $(C_4H_5O_2)'$. These different compounds are liable to be obtained mixed in every proportion (*Phil. Trans.* 1860), so that the difficulties of the investigation are sufficient to discourage even the most practised skill, and often to baffle all the resources of analysis.

† Hofmann has shown that there is no limit to the number of atoms of ammonia which may be thus welded into one, and he has indeed succeeded in grouping together as many as eight atoms of ammonia into one atom of a compound base. The mode in which he has effected this will be readily understood from the symbols which follow:—



$$\mathrm{N}\left\{\begin{array}{l}\mathrm{H}\quad\overbrace{(\mathrm{C_4}\\ \mathrm{H\ H}\\ (\mathrm{C_4H_4})''\end{array}\right\}\mathrm{N\ N}\left\{\begin{array}{l}\mathrm{H_4})''}\quad\overbrace{(\mathrm{C_4}\\ \mathrm{H\ H}\\ \underbrace{(\mathrm{C_4H_4})''}\end{array}\right\}\mathrm{N\ N}\left\{\begin{array}{l}\mathrm{H_4})''}\ \mathrm{H}\\ \mathrm{H\ H}\\ \underbrace{(\mathrm{C_4H_4})''}\end{array}\right\}\mathrm{N}$$

In the formula just given six atoms of ammonia are represented, placed side by side, all linked together into one molecule by the five atoms of the dibasic radicle ethylene.

$$2\,H_3N + \overbrace{(C_4H_4)^{\prime\prime}Br_2}^{\text{Bibromide of ethylene.}} = \overbrace{[(C_4H_4)^{\prime\prime}H_4,N_2]^{\prime\prime}\,2\,HBr}^{\text{Hydrobromate of ethylenia.}};$$

$$4\,H_3N + 2\,[(C_4H_4)^{\prime\prime}Br_2] = \overbrace{[(C_4H_4)_2^{\prime\prime}H_2,N_2]^{\prime\prime}\,2\,HBr}^{\text{Hydrobromate of diethylenia.}} + 2\,H_4NBr.$$

(1197) Diethylenia is a base which was discovered about the same time by Cloez and by Natanson, and was named *acetylia*; but its true nature was first explained by Hofmann.

Hydrated Oxide of Diethylenium $[(C_4H_4)_2^{\prime\prime}H_4N_2O_2,2\,HO.]$—When Dutch liquid $(C_4H_4Cl_2)$ is heated for some hours to a temperature of 300° in a sealed tube, with about 5 times its bulk of a concentrated solution of ammonia, it is completely decomposed; a yellow liquid is formed, and crystals of chloride of ammonium are deposited in abundance: if these be separated by filtration through muslin, and the mother liquor be treated with oxide of silver, it yields a decidedly alkaline solution, which absorbs carbonic acid from the air. The new base thus obtained is not volatile, its salts have a feebly acid reaction, and do not crystallize. If its chloride be mixed with a solution of bichloride of platinum it yields a wax-like mass, which has the composition of the double chloride of platinum and diethylenium $[(C_4H_4)_2^{\prime\prime}H_4N_2Cl_2,2\,PtCl_2]$. Chloride of diethylenium, if slightly acidulated with sulphuric acid and mixed with nitrite of silver, furnishes aldehyd in abundance:—

$$\overbrace{(C_4H_4)^{\prime\prime}_2H_4N_2Cl_2}^{\text{Chloride of diethylenium.}} + 2\,(AgO,NO_3) = 2\,\overbrace{C_4H_4O_2}^{\text{Aldehyd.}} + 2\,N_2 + 2\,H_2O_2 + 2\,AgCl.$$

This reaction corresponds to that of nitrous acid on ethylia, by which alcohol is reproduced, whilst nitrogen and water are liberated.

It may be remarked that hydrated oxide of diethylenium is metameric with aldehyd-ammonia, although so different from it in properties:—

$$\overbrace{(C_4H_4)_2^{\prime\prime}H_4N_2O_2,\,2\,HO}^{\text{Hydrated oxide of diethylenium.}} = \overbrace{2\,(C_4H_4O_2,H_3N.)}^{\text{Aldehyd-ammonia.}}$$

Diethylenia $(C_4H_4)_2^{\prime\prime}H_2N_2$; *Sp. gr. of liquid* 0·975; *of vapour* 1·522; *Boiling pt.* 338° (Hofmann).—If an alcoholic solution of the hydrated oxide of diethylenium be distilled to dryness in a retort, and the temperature be then raised to about 300°, water again begins to escape, and at a temperature of 428° yellowish oily drops of diethylenia pass over. This body has a peculiar persistent odour, which is ammoniacal, and at the same time *recals* that of aldehyd. It does not become solid at —13°. It is inflammable, and burns with a bluish white flame. It is insoluble in ether, but freely soluble both in water and in alcohol. Sodium exerts no action upon diethylenia at ordinary temperatures. Dry reddened litmus-paper does not become blue even when immersed in it; but if the base be treated with acids it forms salts which are identical with those of oxide of diethylenium. If potash be added to a solution of these salts, the liquid does not emit the odour of diethylenia, but exhibits the properties of a solution of hydrated oxide of diethylenium. An aqueous solution of diethylenia produces in a solution of the salts of zinc, a white precipitate which is soluble in excess of the base. With salts of copper it gives a pale yellow precipitate, which is partially soluble if diethylenia be added in excess, forming a bright blue liquid. It occasions a white precipitate in solutions of the salts of silver, but the precipitate is readily dissolved by an excess of the base, and if the solution be gently warmed, a mirror-like coating of reduced silver is formed on the sides of the vessel.

It is remarkable that the oxide of diethylenium should be so permanent a body as to require a temperature of 300° for its decomposition, although the corresponding compound of ammonium undergoes decomposition as soon as it is formed at ordinary temperatures. Diethylenia corresponds exactly with two atoms of ammonia, and like it does not form salts until it has assimilated the elements of water.

Cloez believed that formyl also entered into the composition of a base (C_2H,H_2N; *Boiling pt.* 253·4; *Sp. gr. of vapour* 2·00) termed *formylia*, homologous with acetylia; but Hofmann appears to have proved that this base contains one atom of hydrogen more than that given in the formula, and that it is really *ethylenia* $(C_4H_4)''H_4N_2$. The careful examination which these bodies are now undergoing will doubtless soon clear up several points respecting their true constitution, which are still in dispute.

If diethylenia be treated with iodide of ethyl, *diethyl-diethylenia* is obtained, a base which is represented by the formula $(C_4H_4)_2''(C_4H_5)_2N_2$. *Diphenyl-diethylenia* $(C_4H_4)_2''(C_{12}H_5)_2N_2$ is procured by treating Dutch liquid with aniline instead of with ammonia:—

$$2\,\overbrace{C_4H_4Cl_2}^{\substack{\text{Dutch}\\\text{liquid.}}}+4\,\overbrace{C_{12}H_7N}^{\text{Aniline.}}=2\,\overbrace{C_{12}H_7N,HCl}^{\substack{\text{Hydrochlorate}\\\text{of aniline.}}}+\overbrace{(C_4H_4)_2''(C_{12}H_5)_2N_2,\,2\,HCl}^{\substack{\text{Hydrochlorate}\\\text{of diphenyldiethylenia.}}}.$$

Corresponding bodies may be obtained by treating Dutch liquid, or dibromide of ethylene, with methylia, ethylia, and other analogous bases.

Diethylenia also produces compounds corresponding to the amides. Thus, when butyric ether is mixed with an alcoholic solution of diethylenia, crystals of *butyric diethylenamide* $\left.\begin{matrix}(C_8H_7O_2)_2\\(C_4H_4)''_2\end{matrix}\right\}N_2$ are formed.

5. *Bases produced by the action of Ammonia on certain Aldehyds among the Essential Oils.*

(1198) During the process of obtaining formic acid by distilling bran or oatmeal with peroxide of manganese and dilute sulphuric acid, a small quantity of an essential oil distils over, which may be purified by redistillation.* To this body the name of *furfurol* ($C_{10}H_4O_4$; *Sp. gr. of liquid* 1·168; *of vapour* 3·34; *Boiling pt.* 323°) has been given. When pure it is colourless, but it quickly becomes brown by exposure to the air. It has a fragrant odour, somewhat resembling that of bitter almonds. It is dissolved by cold sulphuric acid, forming a beautiful purple liquid, from which on dilution with water the oil is separated unchanged.

Schwanert (*Liebig's Annal.* cxvi. 260) has verified the conjecture of Gerhardt, that furfurol is the aldehyd of pyromucic acid. Like the aldehyds it combines with bisulphite of soda. If an aqueous solution of furfurol is boiled with freshly precipitated oxide of silver, metallic silver is deposited, and the hot filtrate on cooling deposits small crystals of pyromucate of silver:—

$$\overbrace{2\,C_{10}H_4O_4}^{\text{Furfurol.}} + 3\,Ag_2O_2 = 2\,(\overbrace{AgO,C_{10}H_3O_5}^{\text{Pyromucate silver.}}) + 2\,Ag_2 + H_2O_2.$$

In this way furfurol, by combining with two atoms of oxygen, becomes converted into pyromucic acid.

If furfurol be mixed with a solution of ammonia in the cold, it is gradually converted into a solid yellowish-white insoluble mass, 3 molecules of furfurol reacting upon 2 of ammonia, while 6 atoms of water are separated; $3\,C_{10}H_4O_4 + 2\,H_3N = 2\,C_{15}H_6NO_3 + 3\,H_2O_2$. This new compound belongs to the class of hydramides (1168); it has been termed *furfuramide*. Acids ately decompose it; a salt of ammonia is formed, and is set at liberty. When boiled with potash, however, monia is evolved; the substance is completely dissolved, solution on cooling deposits long silky needles of a power-kaline base which is isomeric with furfuramide (Fownes).

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* Furfurol is best obtained by digesting the bran in a cold dilute solution of caustic potash to dissolve out the gluten and starch, washing well, and drying at a gentle heat, then mixing it with half its weight of sulphuric acid, which must be first diluted with an equal bulk of water. The pasty mass thus obtained is distilled in a current of steam: the furfurol comes over dissolved in the water, from which it may be recovered by distillation, collecting *the first* half only, and again submitting that to a like process of partial *distillation.*

fúria or *furfurine* ($C_{30}H_{12}N_2O_6=268$), as this base has med, is inodorous and sparingly soluble in water; alcohol her dissolve it freely. It melts below 212° to an oily liquid. It is dissolved by dilute acids, and completely izes them; on adding ammonia to these solutions, the is precipitated unchanged. Its salts have a bitter taste; re said to have been used medicinally, with success, as ites for those of quinia (Gregory).

zoline or *amarine* ($C_{42}H_{18}N_2$).—When a solution of ammonia ed to remain for some days in contact with pure hydride oyl (essential oil of bitter almonds), a reaction occurs us to the foregoing one with furfurol: the mixture ly becomes converted into a crystalline mass of hydro-ide; this substance is soluble in alcohol, but insoluble in If boiled with a solution of potash it assumes the appear- a resin, and becomes changed into *benzoline*, which is a meric with hydrobenzamide. The same change occurs if nzamide be simply heated for some time to a temperature 250° and 265°. If the mass which is obtained by either methods be treated with boiling alcohol, it is dissolved, solution on cooling deposits the base in brilliant ent four-sided prisms, which are fusible below 212°. ie is nearly insoluble in water, but it is readily dissolved alcohol and ether. Its salts, with the exception of the are sparingly soluble, and have an intensely bitter taste. enzoline is submitted to destructive distillation, a new ne body, *pyrobenzoline* or *lophine* ($C_{42}H_{17}N_2$)? is formed, other products.

B. NATURAL BASES.

1. *Volatile Oily Bases destitute of Oxygen.*

99) CONIA or *Conylia* ($C_{16}H_{15}N=125$; *Sp. gr. of liquid* 0·89, *pt.* 340° (Blyth)), is the active principle of the hemlock *maculatum*); it pervades the whole plant, but is most ned from the seeds. As it is volatile, it is obtained by mlock seeds with water which contains a small quantity solution; conylia then passes over with the water in

the form of a yellowish oil. When purified by redistilla
is a colourless, transparent, volatile, oily liquid. It has
penetrating, most unpleasant and oppressive odour,
the fresh hemlock. A drop of it, when placed upon pap
a temporary greasy stain. It is soluble to some exte
but is much less so in hot than in cold water; ether
dissolve it freely. Its vapour is inflammable.

According to Kekulé and Planta there are two
varieties of conylia contained in the plant; viz. *conylia*
and *methylconylia* ($C_{18}H_{17}N$); when either of these bas
upon by iodide of ethyl or of methyl, new substitution
obtained, furnishing the following series of compounds

Conylia . . . $C_{16}H_{15}N = H(C_{16}H_{14})''$
Methylconylia . $C_{18}H_{17}N = C_2H_3(C_{16}H_{14})'$
Ethylconylia . . $C_{20}H_{19}N = C_4H_5(C_{16}H_{14})'$
Hydrated oxide ethyl-methyl-conylium $C_{22}H_{22}NO,HO = C_4H_5,C_2H_3(C_{16}H_{14})''$

These experiments show that conylia must be r
an imide base from which ammonium bases may be pr

When normal conylia ($C_{16}H_{15}N$) is exposed to
rapidly absorbs oxygen; first becoming brown, and
nearly solid. Conylia has a powerfully alkaline r
neutralizes the acids perfectly, and precipitates ma
metallic oxides from their salts; in all its forms it
dangerous poison. Its salts crystallize with difficult
solutions are evaporated in the air, they are decompose
red or violet in colour, and ultimately assuming a dark
blue tint. Strong sulphuric acid causes its compounds
first of a purple red colour, and then of an olive gre
nitric acid it gives a blood-red colour, fading into oran
acid is one of the products of this reaction. Conylia
cyanic ether, and immediately forms a compound urea:

$$\overbrace{C_4H_5O,C_2NO}^{\text{Cyanic ether.}}+\overbrace{C_{16}H_{15}N}^{\text{Conylia.}}=\overbrace{C_{22}H_{20}N_2O_2}^{\text{Ethyl-conyl-urea.}}, \text{ or } \left.\begin{array}{l}(C_2\,O_2)'' \\ (C_{16}H_{14})'' \\ C_4\,H_5 \\ \quad H\end{array}\right\}$$

Wertheim finds that hemlock contains, in addition
a small quantity of another base, *conydrin* ($C_{16}H_{17}NO_2$
Annal. c. 328), which contains the elements of 2 a
water than conylia, and which, by distillation with
anhydride, may be converted into conylia; the latt

ed from the phosphoric acid by treatment with potash. drin is much less poisonous than conylia. It may be sub- d in beautiful colourless needles, which are freely soluble in hol and ether; it is strongly alkaline.

(1200) SPARTEIA ($C_{16}H_{13}N$; *Boiling pt.* 550°).—In the *Spartium* rium, or common broom, Stenhouse discovered an oily base, hich he gave the name of *sparteine*. It possesses narcotic erties, is considerably heavier than water, and has a faint r recalling that of aniline; when pure it is colourless, but it ally becomes brown by exposure to the air. With bichloride latinum, and with corrosive sublimate, it forms double chlorides, h crystallize readily: but its other salts are obtained in tals with difficulty. The hydrochlorate appears to undergo al decomposition, if boiled with excess of hydrochloric acid, it emits an odour like that of mice. Both the base and its have an extremely bitter taste. Sparteia contains 2 equiva- of hydrogen less than conylia. The broom plant also fur- es a neutral, yellow, crystallizable principle, termed *scoparin* $H_{11}O_{10}$), to which its diuretic properties appear to be owing.

1201) NICOTYLIA or *Nicotine* [$(C_{10}H_7)_2'''N_2$] or $(C_{10}H_7)'''N$]; r. *of liquid* 1·027 at 66°; *of vapour* 5·607; *Boiling pt.* 480°.— is another remarkable volatile base, which is destitute of gen. From the specific gravity of its vapour it is necessary egard it as a diatomic base, the quantity, $C_{20}H_{14}N_2$, being valent to 4 volumes. It must therefore be formed upon the of 2 atoms of ammonia, and it saturates 2 equivalents of a asic acid. Nicotylia is the active principle of the tobacco (*Nicotiana tabacum*), in which it occurs in combination with and citric acids. It is also contained in the smoke of the g leaves. Nicotylia is a limpid, colourless, oily liquid, with tremely irritating and powerful odour of tobacco. It is inflammable, and burns with a smoky flame. It may be led readily along with the vapours of water, or in a current ydrogen gas; though its boiling point is as high as 480°. posed to the air it absorbs oxygen, becoming brown, and ately solid. Nicotylia is very soluble in water, and in the oils; it is also soluble in all proportions in alcohol and

Ether, if agitated with the aqueous solution, extracts the of the alkali; and the ethereal solution rises to the surface the two liquids are left at rest. Nicotylia is extremely nous, a single drop of it being sufficient to kill a large dog. rts left-handed rotation on a polarized ray. Its solution a white precipitate in a solution of corrosive sublimate, as

well as in one of acetate of lead, and of both the chlorid
The white precipitate which it occasions in solutions of
of zinc is soluble in excess of nicotylia. Salts of copper,
excess of nicotylia, yield a blue solution, like that which
nish when supersaturated with ammonia.

Chlorine acts powerfully upon nicotylia, producing
blood-red liquid. Iodine forms with the alkali a cr
combination $[(C_{10}H_7N)_2I_3]$ which has a ruby-red colour
decomposes this compound, liberating pure nicotylia. Th
nicotylia crystallize with difficulty: they are neutral, and
soluble in water and alcohol, but insoluble in ether,
exception of the acetate. The proportion of this alk
greatly in different samples of tobacco. French tobacco
7 or 8 per cent.; Virginia, 6 or 7 per cent.; and Maryl
Havannah, not more than 2 per cent., which is the prop
ordinary snuff.

Nicotylia appears to belong to the class of nitrile ba
hydrocarbon *nicotyl* $(C_{10}H_7)'''$ which it contains, being e
in function to the 3 atoms of hydrogen in ammonia. T
enters into direct combination with iodide of ethyl,
iodide of methyl; forming compounds which correspon
iodide of tetrethylium; and when these compounds ar
with recently precipitated oxide of silver, they yield a p
alkaline, inodorous, very bitter substance, which rapidl
carbonic acid from the air; for example:—

$$\overbrace{(C_{10}H_7,C_4H_5,N)_2I_2}^{\text{Iodide of ethylnicotylium.}}+2\,(AgO,HO)=\overbrace{[(C_{10}H_7)'''C_4H_5,N]_2O_2,2\,HO}^{\text{Hydrated oxide of ethylnicotylium.}}$$

(Kekulé and Planta, Liebig's *Annal.* lxxxvii. 1.)

The best process for preparing nicotylia is that em
Schlœsing. He evaporates the aqueous infusion of toba
to the consistence of syrup, and adds twice its volume
of sp. gr. 0·837. The liquid is thus separated into tw
the upper one, which contains the salts of nicotylia, is
concentrated by evaporation, mixed with a solution of po
briskly agitated with ether. The ether dissolves the
nicotylia and some fatty matters, and rises with them
surface when the mixture is left at rest. In order to p
alkali, powdered oxalic acid is added by degrees to the
ethereal solution. The oxalate of nicotylia, being ins
ether, forms a dense syrupy layer at the bottom of th
It is washed two or three time with pure ether; and the
is separated by the addition of a fresh quantity of so

and ether. The ethereal solution is decanted into a retort, d with the means of transmitting a current of dry hydrogen h it; the ether is then driven off, and the residue exposed nty-four hours to a temperature of 284°, in order to expel t traces of ammonia and ether; after which the tempera- raised to 356°, when the nicotylia distils over in a state ty.

02) *Preparation of Snuff.*—A full account of this operation, ormed at the Imperial tobacco works in Paris, is given by and Fremy (*Traité de Chimie*, 2nd ed., iv. 437). The ng is an outline of the steps of the manufacture:—The r kinds of tobacco are those which are preferred for the tion of snuff. The leaves are spread out in thin layers stone pavement, and moistened with about a fifth of their of a solution of chloride of sodium in water (sp. gr. 1·089). istened leaves are next cut into blocks, and are then piled large rectangular heaps, in quantities of 40 or 50 tons. nasses gradually enter into fermentation, and the tempe- rises sometimes as high as 170°, but usually it does not 140°. If the temperature be allowed to rise too high, arts of the mass become black, as though they had been . Spring and autumn are the seasons most favourable for mencement of this operation, which requires careful watching ent the development of heat from becoming excessive. In ive or six months the temperature becomes stationary, or to decline; the heaps are then opened out, and the fer- l mass is submitted to grinding. The pale brown, and atively dry powder thus obtained, is next mixed with about nths of its weight of the solution of chloride of sodium, passed through a sieve, to ensure a uniform moistening mass; after which it is packed in large oaken chests, of containing from 25 to 50 tons of the material. Here ff remains for nine or ten months, and undergoes a second tation, in the course of which the temperature in the of the mass rises to 120° or 130°. During this process ff acquires its well-known dark colour, and the aroma is ed. The mass is, however, still far from uniform in , throughout; it is therefore transferred to a second in which operation all the different parts of the heap are ghly mixed together; after the lapse of two months, it is a time turned over, and, sometimes, a third transfer is deemed te. When considered ripe, the contents of the various are mixed in a large room capable of containing 350 tons

of snuff. Here it is left for about six weeks, to ren
entire mass uniform in quality; and finally it is sifted into
for the market. The whole process of manufacture thus
from eighteen to twenty months. During the fermentatio
two-thirds of the nicotylia is destroyed. A small portion
base appears to exist in snuff, in the uncombined form;
greater part of the portion still remaining, is left in the
acetate, a certain amount of acetic acid having become d
during the fermentation. A portion of the decomposed
undergoes conversion into carbonate of ammonia, which
tially retained by the snuff; and the gradual volatiliz
this salt appears to favour the conversion of nicotylia into
and thus to occasion the pungent odour for which snuff is
The proportion of citric and malic acids becomes diminishe
the fermentation; so that ordinary snuff has an alkaline
A certain quantity of a peculiar essential oil appears al
developed during the operation; and to the variable propo
this oil, much of the difference in the flavour of the differe
ties of snuff is owing. The quantity of nitrate of potas
fresh tobacco contains, passes over, unaltered, into the sn

It may be remarked, that tobacco is one of the most
ing crops which can be grown upon any soil, since it carri
enormous amount of mineral constituents (the proportion
amounting to not less than 21 per cent. of the dry leaf).
these constituents, nitric acid is found in quantity often e
2 per cent. of the dry leaf; whilst the salts of potash a
more than a third of the saline residue.

It is probable that the active principle of henbane or
amus niger, is a volatile base, analogous to nicotylia;
portion of some volatile base comes over when the plant
tilled with a solution of potash. Much of the alkaloid,
is decomposed in this operation: its composition has
determined.

2. *Bases which contain Oxygen.*

(*a*) *Alkaloids of the Cinchonas.*

(1203) In the bark of the different varieties of
several well characterised and important bases occur.
all closely related to each other in composition, and are
combination with quinic and quinotannic acids, in the bar
most abundant of these bodies are *cinchonia* and *quinia*,
which is accompanied by, or is convertible into, two isome
termed respectively, *cinchonidine* and *cinchonicine*, and

and *quinicine*. Besides these, a base termed *aricine*, or *cinchovatine*, has been found in the bark of the *Cinchona ovata*. Until recently it was supposed that the formula of cinchonia was $C_{20}H_{12}NO$, and that of quinia $C_{20}H_{12}NO_2$; but the researches of Strecker appear to indicate that these formulæ must be doubled. Both cinchonia and quinia form two classes of salts; one class of which has been regarded, until quite recently, as being basic, whilst the other was supposed to be normal: the common medicinal sulphate of quinia, for example, was viewed as the basic sulphate. If the formula of the base be doubled, however, this salt will be normal, whilst that formerly regarded as normal must be an acid salt. The salts which these bases form with the smaller proportion of acid are very sparingly soluble in water, but are readily dissolved on the addition of any free acid.

Quinia and cinchonia, as well as cinchonidine, appear to belong to Hofmann's class of nitrile bases; since, when treated with iodide of methyl, or with iodide of ethyl, they yield bases of the ammonium type. Hydrated oxide of *ethyloquinium* $[2(C_{20}H_{12}NO_2),C_4H_5O,HO]$ is a powerful base, which attracts carbonic acid from the air: the iodide of *methyloquinium* consists of $2\ (C_{20}H_{12}NO_2),\ C_2H_3I$. The iodides of the corresponding derivatives of cinchonia and cinchonidine, each consist of $2\ (C_{20}H_{12}NO),\ C_2H_3I$. Induced by these and other circumstances, Strecker doubles the old formula of these alkaloids, representing quinia as $C_{40}H_{24}N_2O_4$.

Cinchonia and quinia, with their isomerides, are decomposed when distilled with hydrate of potash. Several volatile bases are formed, amongst which quinoline (1067) is the most abundant; and formiate of potash is left in the retort.

Cinchonia and its isomeric congeners, are most abundant in the pale Peruvian bark. Quinia, and its isomeric companions, occur most abundantly in the yellow bark, or *Cinchona cordifolia*; whilst the red bark contains both classes of alkaloids.

Quinia, from its febrifuge and antiperiodic powers, is the most highly esteemed of these alkaloids for medicinal purposes; though it appears that quinidine possesses similar therapeutic virtues to a nearly equal extent.

(1204) 1. CINCHONIA ($C_{40}H_{24}N_2O_2=308$) crystallizes in large quadrilateral prisms, which are anhydrous; it is less soluble in alcohol than quinia, and is insoluble in ether. Cinchonia is dissolved by solutions of the alkalies and alkaline bicarbonates. At 329° it fuses to a colourless liquid, which becomes a crystalline mass on cooling; when heated further it is partially volatilized; but a portion, at the same time, undergoes decomposition. It may be sublimed, readily, in an atmosphere of hydrog salts are intensely bitter; they are precipitated by infusion as well as by solutions of the oxalates, tartrates, and g Two equivalents of the hydrogen in cinchonia may be di by chlorine, and by bromine: the new compounds thus c retain their basic characters.

Sulphate of cinchonia ($2\ HO, 2\ C_{40}H_{24}N_2O_2,S_2O_6+4$ 714+36) crystallizes in irregular prisms, which melt, lik at a little beyond 212°; when gently heated, it emits phorescent light. If it be first moistened with water aci with sulphuric acid, it may be kept in a fused condition fo hours; during which time it gradually passes into the sulp cinchonicine (Pasteur). If heated more strongly it is co into a resinous mass, of a beautiful red colour. The *Bi* ($2\ HO,C_{40}H_{24}N_2O_2,S_2O_6+6\ Aq$) is very soluble both in and in alcohol; it crystallizes from a hot solution, in larg defined, rhombic octohedra. When cinchonia is dissol sulphuric acid, and heated with peroxide of lead, it prod red-coloured compound; when mixed with chlorine wat afterwards with ammonia, no green tint is produced, as when quinia is similarly treated. Its salts are generally soluble both in alcohol and in water, than those of quinia.

2. *Cinchonidine* ($C_{40}H_{24}N_2O_2$).—This alkali, which is i with cinchonia, occurs naturally in certain varieties of ci bark; and may be obtained by the spontaneous evaporation alcoholic solution, in hard, brilliant, striated, rhomboidal which are anhydrous, and insoluble in ether. Its solu absolute alcohol produces left-handed rotation upon a po ray; whilst cinchonia produces rotation to the right. Cin dine fuses at 347°, and, at a higher temperature, is decom emitting an odour of oil of bitter almonds.

When the solutions of the salts of this base are mixed w caustic alkalies, or with the carbonates or bicarbonates o bases, they give a white precipitate of cinchonidine, which gr becomes crystalline. Phosphate of soda, corrosive sub nitrate of silver, and sulphocyanide of ammonium, also giv precipitates in solutions of salts of cinchonidine. At temperature, the salts of cinchonidine pass into those of cin cine. The *Sulphate* [$2\ (C_{40}H_{24}N_2O_2HO)\ S_2O_6$] crystalli stellate groups of silky needles, the solution of which is to test papers. The hydrochlorate crystallizes in large, br rhomboidal prisms, soluble in about twenty-seven parts of

3. *Cinchonicine* is a third base, which has the same

as the two foregoing ones. It is precipitated from its salts
e form of a resinous mass, which is freely soluble in alcohol.
solution causes right-handed rotation of a ray of polarized
. Cinchonicine is best prepared by the action of heat upon
ulphate of cinchonia, in the manner already mentioned.

205) 4. Quinia ($C_{40}H_{24}N_2O_4+6$ Aq=324+54) is most abun-
in the yellow bark (*Cinchona cordifolia*), in which it occurs
d with cinchonia, and combined with quinic and quinotannic
. The quantity of the alkaloids varies in different specimens
rk, but the two together generally amount to 3·5 or 4 per
In order to extract the bases, the pulverized bark is boiled
8 or 10 times its weight of water acidulated with 1 per cent.
l of vitriol, or with 2 per cent. of hydrochloric acid. The
d is strained through a cloth, and the residue is boiled twice
acidulated water. When the strained liquors are cold, milk
ne, or carbonate of soda, is added in slight excess; the precipi-
is submitted to pressure, and then treated with hot alcohol.
e proportion of cinchonine be considerable, it crystallizes as
quid cools; and a fresh quantity is obtained by distilling off
alf of the alcohol from the residue, whilst the quinia remains
lution: the liquid is then neutralized with sulphuric acid.
eparation of the two bases is afterwards completed by crystal-
the mixed sulphates from a slightly acid solution; the
ate of quinia being much the less soluble of the two, crystal-
first. The alkaloid is then thrown down from the sulphate
ding ammonia. Cinchonia and cinchonidine may also be
ated from quinia, by means of ether, which dissolves the
a, and leaves the cinchonia and cinchonidine.

uinia may be obtained in crystals, though with some difficulty,
owing its alcoholic solution to evaporate spontaneously in a
lace: silky needles are thus formed; they are dissolved
more readily by cold alcohol than the crystals of cinchonia.
requires about 350 parts of water for its solution. By a
of 240°, 6 equivalents of water are expelled, and at a little
this point the alkali fuses into a resinoid mass, which may
tilled in great part without decomposition. Quinia is also
le both in the essential and in the fixed oils.

Quinia yields crystallizable salts; but when these salts are
ed in solution to a strong light, or when they are treated
an excess of acid, they pass into a resinoid amorphous
tion, and constitute the substance met with in the shops as
line, which is also contained abundantly in the mother
rs from which the salts of quinia have been crystallized. The

employment of an excess of acid in extracting the alkali from the bark should be avoided, since it appears to increase the formation of this uncrystallizable substance. Quinoidine is a mixture of several basic compounds, among which are all the alkaloids of the cinchona bark. In some instances as much as 50 or 60 per cent. of crystallized quinidine have been extracted from it by treatment with ether. Pasteur considers that the production of quinoidine might be greatly diminished if more care were taken in drying the bark upon the spot where it is collected. Exposure to the sun's rays should be avoided, for it is found that direct sunlight has a remarkable influence in producing the change of the crystallizable alkaloids into the uncrystallizable form.

The salts of quinia have an intensely bitter taste; they give abundant precipitates with tincture of galls, with nitrate of red oxide of mercury, and nitrate of silver,—also with gallic, tartaric, and oxalic acids, and their salts. If quinia be suspended in water, and chlorine be transmitted through the liquid, the alkali is dissolved, and the solution passes successively through various shades of rose, violet, and dark red. The following reaction is regarded as characteristic of quinia and its metamerides: when freshly prepared chlorine water is poured into a solution of one of the salts of this alkali, and then a few drops of ammonia are added, a green colour is produced.

The presence of cinchonia in the salts of quinia may be detected in several ways; one of the best is that proposed by Liebig: 10 grains of sulphate, or other salt of quinia suspected to be impure, are placed in a test tube with 2 drachms of washed ether, and 20 drops of a solution of caustic ammonia are added. The mixture is briskly shaken, and, on standing, it separates into two layers, the upper one consisting of an ethereal solution of quinia, the lower one of an aqueous solution of sulphate of ammonia; the cinchonia being insoluble in either liquid floats upon the surface of the watery layer. The fraudulent admixture of salicin with the salts of quinia is detected by the addition of a few drops of oil of vitriol to the salt; if salicin be present it gives a red colour to the mixture.

The *sulphate of quinia*, usually called the *disulphate*, [$2\ (HO,C_{40}H_{24}N_2O_4)S_2O_6 + 14\ Aq = 746 + 126$], is the salt employed in medicine: it crystallizes in snow-white, very light, bulky, efflorescent needles, which are sparingly soluble in water, but abundantly so in dilute sulphuric acid and in alcohol. The acidulated solution shows the phenomenon of fluorescence (104) in a striking manner. Sulphate of quinia fuses easily on the aplication of heat, and emits a phosphorescent light. An *acid sulphate* ($C_{40}H_{24}N_2O_4$, 2 $HO,S_2O_6 + 14$ Aq) may be obtained by dissolving the foregoing salt in sulphuric acid, and concentrating the liquid; it crystallizes in small needles, which are freely soluble in water, and in alcohol.

A remarkable compound of iodine and sulphate of quinia ($C_{40}H_{24}N_2O_4I_2$, 2 $HO,S_2O_6 + 10$ Aq) has been described by Dr. Herapath. It may be obtained by dissolving the bisulphate of quinia in concentrated acetic acid, and adding to the heated liquid an alcoholic solution of iodine, drop by drop. After standing for a few hours, the salt is deposited in large flat rectangular plates, which when seen by reflected light are of a brilliant green colour, with a metallic lustre, like the wing-cases of the blistering beetle. When viewed by transmitted light they appear of a pale olive tint, but the light so transmitted is perfectly polarized; so that if a second plate cross the first at right angles, the whole of the light is as completely arrested by the overlapping portions, as it would be by two overlapping plates of tourmaline, the axes of which cross each other at right angles (113). Quinia passes unchanged into the urine, and may readily be detected in this excretion from patients to whom it has been freely administered.

When a solution of sulphate of quinia is boiled with one of nitrite of potash, nitrogen is evolved, and the liquid when mixed with ammonia deposits a white crystalline hydrate of a new base, *oxyquinia*, which, when dried at 302°, consists of $C_{40}H_{24}N_2O_6$; (Schutzenberger). It is much less bitter than quinia, and is fusible into a resinoid mass.

5. *Quinidine* ($C_{40}H_{24}N_2O_4 + 4$ Aq) is a base isomeric with quinia. It is extracted from quinoidine by treatment with ether. The ethereal solution if left to spontaneous evaporation crystallizes with facility, in long rhombic efflorescent prisms. The solution of quinidine in absolute alcohol produces right-handed rotation of a polarized ray (Pasteur), whilst a similar solution of quinine produces rotation to the left (Bouchardat). Quinidine is much less soluble in water than quinia, for it requires about 1500 parts of cold water for solution; but it is much more soluble than quinia in ether. When heated, it loses its water of crystallization, and it fuses at 320°. The acid sulphate of quinidine is much less soluble than the corresponding salt of quinia; whilst the oxalate is freely soluble in water, and may thus be separated from the oxalate of quinia, which is sparingly soluble. Chlorine and ammonia produce a green coloration with the salts of quinidine, similar to that which they occasion with those of quinia.

6. *Quinicine* is produced by the action of heat upon the salts of quinia and quinidine. It is precipitated by alkalies in the form of a fluid resinous mass, which combines readily with acids, and forms bitter uncrystallizable salts, endued with febrifuge properties. These salts are metameric with those of quinia. Quinicine is freely soluble in alcohol: the solution produces right-handed rotation of a ray of polarized light.

The relation of the cinchona alkalies to polarized light is remarkable, and may thus be exhibited :—

Quinia	produces	a powerful left-handed	rotation,
Quinidine	,,	a powerful right-handed	,,
Quinicine	,,	a feeble right-handed	,,
Cinchonia	,,	a powerful right-handed	,,
Cinchonidine	,,	a powerful left-handed	,,
Cinchonicine	,,	a feeble right-handed	,, .

Pasteur considers that quinia and cinchonidine each contain two active groups, one of which produces strong left-handed rotation, the other produces a feeble right-handed rotation. He also regards quinidine and cinchonia as each consisting of two groups; one of which exerts a powerful right-handed rotation, and the other a feeble left-handed rotation; and he supposes that in each of these bases, by the agency of heat, the more powerful group is rendered inert, whilst the weaker one remains unmodified, thus occasioning the effects observed in quinicine and cinchonicine.

7. *Aricine* or *cinchovatine* ($C_{46}H_{26}N_2O_8$).—This base is less abundant than the two alkalies just described. It has been found in a white variety of cinchona bark, and has been but incompletely examined. Aricine crystallizes in white needles, which are fusible at 370°, but not volatile: it is soluble in ether; with nitric acid it strikes an intense and characteristic green colour.

(*b*) *Alkaloids contained in Opium.*

(1206) Opium, the inspissated milky juice of the *papaveraceæ*, is a very complicated substance, the composition of which varies greatly even when it is not adulterated, as it often is very largely. Genuine Smyrna opium is the best variety, since it contains the largest proportion of morphia. The following constituents, with the exception of opianine, have been ascertained to exist in most kinds of opium :—

Meconic acid	$3\,HO,C_{14}HO_{11}$	from 6 to 8 per cent.
1. Morphia	$C_{34}H_{19}NO_6$	from 6 to 12 per cent.
2. Codeia	$C_{36}H_{21}NO_6$	less than 1 per cent.
3. Thebaia	$C_{38}H_{21}NO_6$	ditto.
4. Papaverine	$C_{40}H_{21}NO_8$	ditto.
5. Opianine	$C_{42}H_{21}NO_{14}$?	(from Egyptian opium.)
6. Narcotine	$C_{46}H_{25}NO_{14}$	from 6 to 8 per cent.
7. Narceia	$C_{46}H_{29}NO_{18}$	
Meconine (opianyl)	$C_{20}H_{10}\ O_8$	
Resinous matter		4 or 5 per cent.
Caoutchouc		
Essential oil		
Mucilage or gum		

any of the opium bases exhibit a very intimate relation to ther, although as yet the efforts of the chemist to transform one into the other have been without success. Morphia, it e observed, differs from codeia in containing one equivalent f the compound (C_2H_2), although the two bases do not t the close resemblance usually observed between the con- members of a homologous series. Even if the relation were e of ordinary homology, the action of iodide of methyl upon ia might cause the production of codeia, just as dimethylia is ed from methylia by similar treatment; but, instead of this, tion of iodide of methyl upon morphia is attended with the ion of a new base of the ammonium class. Thebaia con- two atoms more of carbon than codeia, and papaverine 1 le more of carbonic oxide (C_2O_2) than thebaia, whilst e, if Gerhardt's interpretation of the results of Hinter- be admitted, contains 2 atoms of carbon and 6 of oxygen han papaverine.

ianine has hitherto only been found in Egyptian opium, been but imperfectly examined.

e formula of narceia, as given by Anderson, differs from that nary narcotine, in containing 4 atoms more of water.

e opium alkalies, morphia, codeia, and papaverine, combine with iodine, and form crystallizable compounds containing equivalents of iodine to one of the alkali. Codeia also with two atoms of cyanogen, and forms a new and distinct *cyanocodeia*. True substitution-compounds may also be ed from codeia with the halogens, and with nitric acid, in se one or more atoms of hydrogen are displaced by a ding number of equivalents of chlorine, of bromine, or of of nitrogen.

) *Isolation of the Components of Opium.*—The separation ium bases from each other is a matter of considerable and can only be performed satisfactorily when large

masses of opium are acted upon. The following is an outli
the method to be adopted,—the morphia being first obtain
the process of Robertson and Gregory, and the mother-li
being afterwards treated for the other alkalies upon Ande
plan (*Trans. Roy. Soc. Ed.* xx. 347, and xxi. 204):—

1. *Meconic Acid.*—An aqueous infusion of opium is pr
by mixing several pounds of the drug with three times its
of water, straining the solution through linen, and treati
residue two or three times with fresh portions of water. A
liquid is thus obtained, which is to be concentrated by
ration, and mixed with sufficient chalk to render it neut
solution of chloride of calcium containing a quantity of th
equal to about one-twentieth of the weight of the opiu
ployed, is then to be added. The precipitate which is thu
sioned consists of meconate of lime (1154), and must be se
by filtration.

2. *Narcotine.*—A large amount of narcotine remains
portion of opium which is not soluble in water; it can
tracted by adding acetic acid to the mass, precipitating the
liquid by the addition of ammonia, and purifying the crude
tine by digesting its solution in alcohol with animal charco
recrystallizing.

3. *Morphia.*—The clear liquid filtered from the meco
lime is evaporated till it acquires the consistence of a thi
On cooling, it becomes semi-solid, from the formation of
of hydrochlorate of morphia; this salt may be purified by
tallization, after the strongly coloured mother-liquor ha
separated from it by pressure.

4. *Codeia.*—On further concentrating the mother-liquo
the hydrochlorate of morphia, a fresh crop of crystals is se
which consists of a mixture of the hydrochlorates of morp
codeia. If this be dissolved in hot water, and supersaturat
ammonia, the morphia is precipitated, while codeia rem
solution, mixed with muriate of ammonia. The hot
solution is concentrated by evaporation, and, on the add
potash, the codeia is separated, partly in the form of an o
gradually becomes solid, and partly in crystals which are d
as the liquid cools.

The black mother-liquor from which the hydrochlo
morphia and codeia have been separated, contains the who
remaining bases. It is to be diluted with water, and filte
deposit of resinous matter which are thus got rid of, and
is then to be added as long as a precipitate is occasione

ite (A) contains a large proportion of narcotine and of th small quantities of thebaia and papaverine. The filtrate ains narceia and meconine.

Varceia.—To the filtered liquid (B) a solution of acetate of dded, so long as it occasions a precipitate ; a dirty brown g matter is thus thrown down, and is to be separated by n through a cloth ; the excess of lead is removed by etted hydrogen, and the filtered liquid is concentrated by tion to a syrup, which, on standing, becomes filled with ous silky crystals of narceia ; these may be purified by a crystallization.

Meconine.—The mother-liquor from the narceia is agitated ourth of its bulk of ether, and the ethereal solution is de- this process is repeated upon the aqueous portion, with rtions of ether, so long as the ether becomes coloured. ereal solutions are submitted to distillation, and, on the of water to the residue, a resinoid substance is separated, ich hydrochloric acid extracts a portion of papaverine. dissolved portion, when crystallized from its solution in water, yields needles of meconine.

dditional quantity of Narcotine.—The precipitate (A), which arated by ammonia from the mother-liquors of the mor- l codeia, is at first granular, but if left in the press it soon s into a resinoid mass; in order to prevent this agglo- , it must without delay be broken up and diffused through trained, again pressed, and the washings repeated until off nearly colourless. A portion of the precipitate is then ith rectified spirit, and the liquid filtered while hot; of narcotine are deposited as it cools. The spirituous is then boiled with a fresh portion of the precipitate, same process is repeated until the whole of the pre- has been so treated; the narcotine obtained in this can be added to that already procured from the undis- nass (2).

Thebaia.—The spirituous mother-liquor from which the e has crystallized, now contains resinous matter, besides aining some narcotine, and nearly all the papaverine and The alcohol is distilled off, the bases are separated from k brown residue by means of acetic acid, and the solution tained is decanted from the undissolved portion. On adding s of basic acetate of lead to the acetic solution, the whole papaverine, narcotine, and resin are precipitated. The f lead is next removed from the supernatant liquid, by the

addition of sulphuric acid, and filtration; and, on then addin
slight excess of ammonia, impure thebaia is thrown down: i
purified by digestion with animal charcoal, and re-crystalliz
from alcohol.

9. *Papaverine.*—The greater part of the papaverine is
tained in the precipitate which is separated from the acetic
tion of thebaia by subacetate of lead. In order to isolate it,
precipitate is reduced to a fine powder, and boiled with alc
The alcohol is distilled off, and the dark brown residue is tr
with dilute hydrochloric acid, and filtered from undissolved r
the solution is then concentrated, and left to spontaneous e
ration; crystals of hydrochlorate of papaverine are thus gr
ally formed, whilst the accompanying narcotine is retaine
solution.

One of the greatest difficulties in the purification of the op
bases upon a small scale, arises from the presence of a pe
resin in the drug; which, though not possessing the prope
either of an acid or of a base, is readily soluble in dilute
and in solutions of potash, but sparingly so in ammonia.
also soluble in alcohol, but insoluble in ether. It is fusible
temperature considerably below that of boiling water. Aq
solutions of opium contain it in considerable quantity, pr
owing to the free acid which is present in the drug. O
addition of ammonia it is precipitated with the morphia
other bases; and, if the solution be heated, the resin fuses;
occasioning the entire precipitate to agglomerate into a re
mass, which assumes the form of a brittle solid on cooling.

(1208) 1. MORPHIA ($C_{34}H_{19}NO_6+2\ Aq = 285+18$).—
base occurs in combination with meconic, and, sometimes,
sulphuric acid. It appears to be the principal sedative
stituent of opium, of which it constitutes from one-seve
one-sixteenth by weight. In large doses it acts as a p
narcotic poison.

Properties.—Morphia (so called from Morpheus, in allu
its narcotic properties) crystallizes generally in short, rect
prisms, with two equivalents of water of crystallization.
gentle heat the water is expelled, and the alkali melts
resinoid substance, which solidifies into a radiated crystalline
on cooling: by a higher heat it is decomposed. Morphia is
in about 1000 times its weight of cold, and in 400 of boiling
the solution has a bitter taste, and changes the yellow co
turmeric paper to brown. Boiling alcohol dissolves it abun
but it is insoluble in ether and in chloroform. Its al

ts a powerful rotation to the left upon a ray of
t. The fixed alkalies and alkaline earths dissolve mor-
change, and deposit it in crystals, as the solutions by
the atmosphere absorb carbonic acid. Ammonia
nore sparingly. Concentrated nitric acid, when ap-
stal, either of morphia or of one of its salts, produces
low or orange colour; and, ultimately, oxalic acid is
mixture of nitric and sulphuric acids colours morphia
n morphia is mixed with iodic, or with periodic acid,
rated, which may be recognised by its brown colour,
lne which it yields on the addition of a solution of
neutral solution of perchloride of iron strikes with
ry characteristic blue colour, which is destroyed by
acid. The salts of morphia give no precipitate with
but a copious curdy one with tannic acid and its salts.
ia is heated to 400°, with hydrate of potash, an alka-
stils over, containing ethylia. The salts of morphia
adily; they are very soluble in water, and in alcohol,
soluble in ether. They have a bitter, disagreeable
eir solution be mixed with tartaric acid, and super-
h bicarbonate of soda, no precipitate is formed.

appears to belong to the class of nitrile bases; since,
with iodide of ethyl, or with iodide of methyl, it
f *ethylomorphium*, or of *methylomorphium*, correspond-
of ammonium. Iodide of methylomorphium has the
$[C_{34}H_{19}(C_2H_3)NO_6,I]$ (How.)

ion.—Several methods are in use for extracting mor-
ium. On the large scale, Robertson's process, as
Gregory, and already described, is generally adopted.
implest and best plans, if the operation be upon a
s that proposed by Mohr; it is founded on the solu-
phia in lime water, and the insolubility of the other
liquid:—Each pound of opium is digested in 3 lb. of
oiled, and the liquid expressed from the undissolved
h is twice similarly treated; ¼lb. of lime is boiled
water, and the mixed opium infusions are added, in
ies at a time, to the milk of lime, which is kept boil-
id is filtered from the residue containing undissolved
other opium alkalies: this residue is twice boiled up
ter. The filtered liquids are mixed, and evaporated
pints, again filtered, heated to boiling, and one
dered sal-ammoniac is added. By this means, the
lized, and the ammonia, as it is liberated, is volati-

lized at the high temperature employed: morphia is pre
immediately, and increases in quantity as the liquid coo
morphia thus obtained is of a deep brown colour. It i
fore, re-dissolved in hydrochloric acid, again treated w
of lime, and a second time precipitated by sal-ammoni
alkaloid, if the solution be dilute, is now deposited in
crystals.

The *Hydrochlorate* ($C_{34}H_{19}NO_6,HCl+6\ Aq=321·5+$
most important salt of morphia; it crystallizes in silky
and is readily soluble in water, especially if it contain a
hydrochloric acid. It is also dissolved freely by alcoh
Acetate was formerly a good deal used in medicine, but i
disadvantage of being slightly deliquescent, and of losing a
its aqueous solution is evaporated. The *Sulphate* [2 (C_{34}
$HO)S_2O_6+10\ Aq$] crystallizes in tufts of colourless prism
Citrate is said to form the basis of the sedative medicin
under the name of the *Black drop*.

(1209) 2. Codeia ($C_{36}H_{21}NO_6+2\ Aq=299+18$; A
—Codeia (from κώδη, a poppy-head) appears, like morph
one of the nitrile bases; since, when treated with iodide
and then with oxide of silver, it yields a powerful alkalin
the ammonium class. It is contained in opium only
proportion, for it does not amount to more than from one-
to one-thirtieth of the quantity of morphia. It has a p
alkaline reaction, and is remarkable as being soluble in
of cold, and in 17 of boiling water: this solution throws
oxides of lead, of copper, of iron, and of several other met
a solution of their salts. If codeia be boiled with less w
is necessary for its solution, it melts beneath the liquid t
looking fluid. Codeia crystallizes from its aqueous so
bold rhombic octohedra. If heated alone, its hydrated
lose 2 Aq, and undergo fusion at 300°. Both ether an
dissolve codeia freely: the ethereal solution, by spo
evaporation, yields fine anhydrous prisms of the alkali.
tions exert left-handed rotation on a ray of polarized lig
caustic alkalies dissolve it but very sparingly: when disti
potash, codeia yields ammonia, methylia, tritylia, and so
compounds still higher in this series of alcohol bases.
of codeia are practically unimportant: they have been
examined by Anderson, and they appear to have a powe
cotic action when taken medicinally: they are not turne
nitric acid, nor blue by perchloride of iron, but are precip
infusion of galls. The hydrochlorate crystallizes with gre

3. *Thebaia,* or *Paramorphia* ($C_{38}H_{21}NO_6$).—This alkali crystallizes from its solution in alcohol or in ether, in square plates of silvery lustre, which have a styptic, acrid taste. It is poisonous when taken internally, and is said to produce tetanic symptoms, resembling those occasioned by strychnia. Thebaia is insoluble in alkaline liquids: it fuses at 257°: concentrated sulphuric acid colours it of a deep red: its salts do not crystallize readily.

4. *Papaverine* ($C_{40}H_{21}NO_8$) is distinguished from the other opium bases by giving with concentrated sulphuric acid a deep blue colour. It is sparingly soluble in cold alcohol, and is deposited from a hot alcoholic solution in small confused crystals.

(1210) 5. *Narcotine* ($C_{46}H_{25}NO_{14}+2\,Aq=427+18$; Blyth; Wöhler).—The quantity of narcotine in opium varies from 6 to 8 per cent.: this body can hardly be said to possess alkaline properties. It is nearly insoluble in water, but is freely soluble in alcohol, and still more so in ether and in chloroform; its ethereal solution, by spontaneous evaporation, yields it crystallized in acicular groups, or in colourless, brilliant right rhombic prisms; these crystals are soluble in the fatty and essential oils, but are insoluble in the caustic alkalies. Solutions of narcotine exert a powerful left-handed rotation upon polarized light: when the solution is acidulated, this rotatory power is reversed, and becomes right-handed. At 340° narcotine fuses, and loses water, and by a higher temperature it is decomposed. Acids dissolve it freely, but the solutions are decomposed by the addition of a large bulk of water: they are precipitated of a bright yellow on the addition of infusion of galls. A mixture of concentrated sulphuric and nitric acids produces a blood-red colour with narcotine and its compounds. Narcotine is less active as a poison than morphia; but, when administered to a dog in a dose of 23 grains, it speedily produced death. The salts of narcotine have a more bitter taste than those of morphia: the chloride and acetate crystallize with difficulty: most of its other salts form gummy compounds, which do not crystallize. The double salts with bichloride of platinum, and terchloride of gold, are, however, easily procured in crystalline scales. Narcotine is contained largely in the portion of opium which remains undissolved when treated with water. If this residue be digested with acetic acid, and the solution be supersaturated with ammonia, narcotine mixed with colouring matter is thrown down: it may afterwards be purified by solution in alcohol, and treatment with animal charcoal. If any of the acid solutions of narcotine be saturated with chloride of sodium, the liquid becomes turbid, and the narcotine is deposited in the course

of a few days, in crystalline masses. This property has som
been taken advantage of, in the separation of narcotine from m
When narcotine is distilled with concentrated hydriodic acid i
rather more than its own weight of iodide of methyl, or 3 at
the iodide for each atom of narcotine. This is indeed a con
mode of procuring iodide of methyl (Matthiessen and Fost

Wertheim believed that he had proved the existence o
homologous narcotines, viz., methyl-narcotine $C_{44}H_{23}NO_{1}$
narcotine $C_{46}H_{25}NO_{14}$, and trityl-narcotine $C_{48}H_{27}NO_{14}$.
thiessen and Foster, however, who examined a large qua
narcotine from various sources, found only one kind, to whi
assigned the formula $C_{44}H_{23}NO_{14}$, or C_2H_2 less than that o
by Wöhler and by Blyth. It does not appear to exert any p
effect upon the animal economy if taken internally.

Narcotine, under the oxidizing influence of bichloride
tinum or of peroxide of manganese, is decomposed, and giv
to some very remarkable compounds (Wohler; Blyth, *Liebig*
l. 1 and 29; Anderson, *Trans. Roy. Soc. Ed.* xx. 359).
pears to split up into a new base, termed *cotarnine*, and into
or into products which are the result of the decomposi
opianyl :—

$$\overbrace{C_{46}H_{25}NO_{14}}^{\text{Narcotine.}}+O_2=\overbrace{C_{26}H_{13}NO_6,2\,H}^{\text{Cotarnine.}}O+\overbrace{C_{20}H_{10}O_8}^{\text{Opianyl.}}.$$

If the oxidation be more energetic, the cotarnine is bro
into *apophyllic acid* ($HO,C_{16}H_9NO_8$), and ethylia; whi
opianyl yields *opianic* and *hemipinic* acids :—

$$2\,\overbrace{C_{20}H_{10}O_8}^{\text{Opianyl.}}+3\,O_2=\overbrace{HO,C_{20}H_9O_9}^{\text{Opianic acid.}}+2\,\overbrace{HO,C_{20}H_8O_{10}}^{\text{Hemipinic acid.}}.$$

Cotarnine contains all the nitrogen of the narcotine. I
fusible acicular crystals, which are sparingly dissolved by
or by a solution of potash; but they are freely soluble in a
ether, and solution of ammonia. Cotarnine is readily obtai
boiling a solution of narcotine in hydrochloric acid, with b
ride of platinum: the liquid becomes of a blood-red colou
red crystals of the bichloride of platinum and hydrochlo
cotarnine ($C_{26}H_{13}NO_6,HCl+PtCl_2$) are deposited: the b
easily procured by decomposing this salt with an alkali.

It will be unnecessary to enter into any minute descri
the properties of the various products obtained by the oxida
narcotine,* for they present but little intrinsic interest,

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* For details upon this subject, *vide* Anderson, Wöhler, and Bly
cit., and Matthiessen and Foster, *Proceed. Roy. Soc.* xi. 55;
chemists give the formula for cotarnine as $C_{24}H_{12}NO_6$.

a knowledge of their composition, and of the mode of their formation, is essential towards the explanation of the rational composition of the group of alkaloids contained in opium.

6. *Opianyl*, or *Meconine* ($C_{20}H_{10}O_8$) may not only be formed by the oxidation of narcotine, but it exists in opium, in small quantity. This substance does not possess basic properties: it is freely soluble in boiling water, and crystallizes in white, inodorous, six-sided prisms, which are sparingly soluble in cold water, but are readily dissolved by alcohol, and ether. It fuses at 194° (230°, Anderson), and may be distilled without alteration. It is soluble in concentrated sulphuric acid, and the liquid becomes purple when gently heated. Gerhardt considers this body to be a *hydride of opianyl*, which stands in the same relation to opianic acid that oil of bitter almonds does to benzoic acid (Gerhardt's opianyl* being $C_{20}H_9O_8$), as is represented by the following formulæ :—

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}}^{\text{Hydride of benzoyl, or oil of bitter almonds.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}O_2}^{\text{Benzoic acid.}} \; .$$

$$\overbrace{\left.\begin{matrix}C_{20}H_9O_8\\H\end{matrix}\right\}}^{\text{Hydride of Opianyl.}} \quad ; \quad \overbrace{\left.\begin{matrix}C_{20}H_9O_8\\H\end{matrix}\right\}O_2}^{\text{Opianic acid.}} \; .$$

Gerhardt's opianyl ($C_{20}H_9O_8$) also appears to enter into the formation of two remarkable compounds, derived from ammonia, which present the composition of amides. Anderson has termed them, respectively, *opiammon* and *teropiammon*: neither of them possesses basic characters :—

$$\overbrace{C_{40}H_{19}N_2O_{16}}^{\text{Opiammon.}} = \left.\begin{matrix}C_{20}H_9O_8\\C_{20}H_9O_8\\H\end{matrix}\right\}N_2 \quad ;$$

obtained by evaporating a solution of opianate of ammonia.

$$\overbrace{C_{60}H_{29}N_2O_{26}}^{\text{Teropiammon.}} = \left.\begin{matrix}C_{20}H_9O_8\\C_{20}H_9O_8\\C_{20}H_9O_8\end{matrix}\right\}N_2, 2\,HO;$$

obtained by the action of dilute nitric acid upon narcotine.

In certain cases, when the oxidation of the narcotine was incomplete, a peculiar platinum salt was obtained by Blyth, which he believed to contain a base termed *narcogenine* ($C_{72}H_{38}N_2O_{20}$), but which he was unable to isolate; since immediately that it is liberated from its combinations, it breaks up into narcotine and cotarnine :—

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* This practice of employing terms already appropriated to previously known substances, *to indicate other compounds*, is greatly to be deprecated.

$$\overbrace{C_{72}H_{38}N_2O_{20}}^{\text{Narcogenine.}} = \overbrace{C_{26}H_{13}NO_6}^{\text{Cotarnine.}} + \overbrace{C_{46}H_{25}NO_{14}}^{\text{Narcotine.}}.$$

(1211) 7. *Narceia*, or *Narceine*.—Two substances appear to have been described under this name; one of these, obtained by Pelletier, having the composition ($C_{32}H_{19}NO_{10}$); the other, examined by Anderson, being ($C_{46}H_{29}NO_{18}$). The latter is a feeble base, which is soluble in boiling water, and crystallizes from a hot solution as it cools, in delicate silky needles, which are soluble in alcohol, but insoluble in ether: at 197° it fuses, and at a somewhat higher temperature it becomes decomposed. It combines with the dilute acids, forming crystallizable salts. Concentrated sulphuric acid dissolves narceine with an intense red colour, which, when gently heated, passes into green. Iodine colours the base of a deep blue, which disappears on the addition of an alkali.

(*c*) *Alkali obtained from the Pepper Tribe.*

(1212) *Piperine* ($C_{34}H_{19}NO_6$; Strecker).—This is a substance possessed of feebly basic properties. It is found in the common white and black pepper, and in long pepper. White pepper easily yields it when treated with alcohol, which extracts a resinous matter with the piperine, from which the latter may be freed by digestion in a solution of potash: the piperine which remains undissolved is recrystallized from alcohol, and furnishes colourless prisms, which are fusible at 212°. Piperine is nearly insoluble in cold water; it has an acrid taste, resembling that of pepper: the hydrochlorate is its most stable salt. Concentrated sulphuric acid dissolves piperine, with a red colour; but the base is precipitated unchanged, on dilution with water. Nitric acid acts powerfully on piperine, developing an odour of bitter almonds, whilst a brown resin rises to the surface. On evaporating the solution to dryness, a brown residue is left, which, when treated with potash, yields a magnificent blood-red liquid; and on distilling this mixture it furnishes *piperidine*, which is a powerfully alkaline base. The same base is also obtained when piperine is distilled with three times its weight of hydrate of potash, at a temperature not exceeding 320°. The piperidine ($C_{10}H_{11}N$), being volatile, passes over, and a yellow, resinoid acid—*piperic acid* ($HO,C_{24}H_9O_7$; Strecker)—remains in combination with the potash; $C_{34}H_{19}NO_6 + KO,HO = KO,C_{24}H_9O_7 + C_{10}H_{11}N$.

Piperidine [$C_{10}H_{11}N = (C_{10}H_{10})''H,N$] *Sp. gr. of vapour* 2·982; *Boiling pt.* about 223°.—This is a remarkable oily base, with a *pungent* odour, recalling both that of ammonia and that of pepper.

It resembles ammonia in alkaline power, and precipitates many metallic oxides from their salts. It combines with the acids, neutralizing them, and forming well crystallized salts: with cyanic acid it forms a compound urea, *piperyl-urea;* and, if heated with cyanic ether, piperidine forms a compound termed *ethyl-piperyl-urea* :—

Urea	H_4N_2,C_2O_2
Piperyl-urea . . .	$H_2(C_{10}H_{10})''N_2,C_2O_2$
Ethyl-piperyl-urea . .	$H,C_4H_5(C_{10}H_{10})''N_2,C_2O_2$

One of the equivalents of hydrogen in piperidine may be displaced by ethyl or by methyl, on treating the base with iodide of ethyl or of methyl; and *ethylo-piperidine,* by treatment with an additional quantity of the hydriodic ether, yields the iodide of an ethyl base corresponding to tetrethylium.

Capsicine is the name given to an alkaloid obtained from the Cayenne pepper. It has a burning taste; and as usually prepared, it presents a resinous appearance; but, when quite pure, it may be crystallized. It forms crystallizable salts with acetic, nitric, and sulphuric acids.

(*d*) *Alkaloids from the Strychnos Tribe.*

(1213) The fruit and bark of the *Strychnos nux vomica,* and other parts of several plants of this tribe, particularly the seeds of the *Strychnos ignatii,* contain two alkalies closely related to each other: both of them act as powerful poisons on the living frame, and speedily occasion death, amid violent tetanic convulsions: these bases are *strychnia* and *brucia.* They contain 2 atoms of nitrogen in each equivalent of base. In the *nux vomica* they occur in combination with lactic acid, and a peculiar vegetable acid. In order to extract them from this fruit, the following method may be adopted:—The rasped seeds are boiled with 4 times their weight of alcohol, acidulated with 1 per cent. of sulphuric acid. The alcoholic liquid is neutralized with lime in slight excess: the acid and colouring matters are thus precipitated, whilst the bases remain in solution; the alcohol is distilled off, and the residue treated with acidulated water, from which, on the addition of ammonia, the strychnia and brucia are precipitated. The two alkalies are separated by converting them into nitrates, and crystallizing; the nitrate of strychnia, being the least soluble of the two, is first deposited. Both strychnia and brucia exert a left-handed rotatory effect upon a ray of polarized light; but the rotatory power of strychnia is twice as great as that of brucia.

(1214) STRYCHNIA ($C_{42}H_{22}N_2O_4=334$) is contained in the S

Ignatius's bean, to the extent of nearly 1½ per cent.; and one of the active constituents of the upas poison. Strych one of the most powerful of the vegetable bases; it precip many metallic oxides from their salts, either completely o tially: in the latter case, it forms double salts,—such double sulphate of strychnia and copper, which crystalli long green needles. Strychnia crystallizes from dilute alco white anhydrous octohedra, or in square prisms, which do no on the application of heat. It is insoluble in absolute al ether, and the caustic alkalies; but it is soluble in the e oils, and in chloroform. Cold water does not dissolve mor than $\frac{1}{7000}$th of its weight; but this solution, even when with 100 parts of water, still possesses a distinctly bitter tast distilled with hydrate of potash, strychnia, like cinchoni quinia, yields the oily base quinoline. A portion of the hyd in strychnia may be displaced by chlorine or by bromine, body thus obtained still retains basic properties. Strychnia, triturated with iodine, forms a peculiar crystalline comp which is soluble in alcohol, and yields orange-coloured $[(C_{42}H_{22}N_2O_4)_2I_3]$, from which the acids separate strychnia, un This compound is analogous to those which iodine yields wi opium bases (1206). Strychnia, when pure, is turned yell concentrated nitric acid, and yields a nitrate of a new substi base, *nitro-strychnia*. If brucia be present with the strych is usual in most commercial specimens, the colour produ nitric acid is deep orange, or red. With iodide of ethyl, str yields the iodide of *ethylostrychnium* $(C_{42}H_{22},C_4H_5,N_2O_4,I)$, which oxide of silver separates a hydrated oxide of an amm base $(C_{42}H_{22},C_4H_5,N_2O_5,HO)$, which is crystallizable: stry is therefore a nitrile base.

Salts of Strychnia.—Sulphuric acid forms a neutral acid salt with strychnia; the crystals of the neutral sulphate $H_{22}N_2O_4,HO)S_2O_6+14\ Aq]$ are square prisms. Solution salts of strychnia yield a precipitate with infusion of galls slight excess of tartaric acid be added to the solution of a strychnia, and then one of bicarbonate of soda or pot strychnia is gradually deposited in crystals. A solution does not contain less than $\frac{1}{375}$th its weight of the base gives addition of a strong solution of sulphocyanide of potassiu of crystals, after the lapse of a few minutes. A minute q of strychnia with concentrated sulphuric acid, and a frag peroxide of lead, or what is still better, of bichromate of gives a beautiful violet tint, which gradually fades into a p r; other oxidizing agents produce a similar effect. With on of perchloride of gold, salts of strychnia give a bright blue r. The presence of strychnia may be detected in very te quantities in complicated organic liquids, by rendering them ine with potash, and agitating thoroughly with a few drachms loroform; the chloroform dissolves the strychnia, and leaves he solid form on evaporation; from this residue it may racted by dilute hydrochloric acid; and it may afterwards be itted to the usual tests.

(1215) *Brucia* ($C_{46}H_{26}N_2O_8+8\,Aq=394+72$; Regnault) is soluble in water, and in strong alcohol, than strychnia. alkali is contained in *nux vomica* in larger quantity than hnia. It may also be readily obtained from the false angus- bark, which does not appear to contain any strychnia, but hes brucia more abundantly than the beans of the *nux vomica.* crystallizes in colourless transparent, oblique rhombic s, which are insoluble in ether. Brucia melts readily on the ation of heat, and loses its water of crystallization. It is ctive as a poison than strychnia. Its salts have a bitter taste, may be distinguished from those of strychnia, after they have mixed with tartaric acid, by not yielding any precipitate on ddition of bicarbonate of soda. This base is further distin- d from strychnia by the bright scarlet colour gradually g into yellow, which brucia or any of its salts gives with acid; if a little protochloride of tin be added, a beautiful colour is produced.

he action of nitric acid upon brucia is attended with the tion of definite results, from which it appears to be probable methyl enters into the composition of this base. When the trated acid is poured upon brucia, the mixture assumes a red colour, becomes hot, and emits a colourless gas, which e peculiar smell of apples, and a portion of which is soluble ter and in alcohol. This gas consists of a mixture of nitrite thyl with binoxide of nitrogen and carbonic acid, the ic acid being the secondary result of the decomposition of acid, which is found in the liquid, accompanied by a new nce termed *cacotheline*; this body is a nitro-substitution- nd, of feebly basic properties. Strecker represents the nitric acid upon brucia by the following equation:—

$$+5\,(\overbrace{HO,NO_5}^{\text{Nitric acid.}})=\overbrace{C_2H_3O,NO_3}^{\text{Nitrite of methyl.}}+2\,\overbrace{HO,C_4O_6}^{\text{Oxalic acid.}}+\overbrace{C_{40}H_{22}(NO_4)_2N_2O_{10}}^{\text{Cacotheline.}}$$
$$+2\,NO_2+2\,H_2O_2.$$

A further proof of the presence of methyl in brucia i in the fact, that when this base is distilled with dilute s acid and peroxide of manganese, or with chromate of pot sulphuric acid, formic and carbonic acids are produced, inflammable liquid passes over, burning with a blue fla presenting the properties of wood spirit.

Igasuria.—This name has been given to a third alkali di in *nux vomica.* It is more soluble in water than either s or brucia.* The *Urari* or *woorara* poison of South appears to be obtained from a plant of the strychnos tribe as a fatal poison if introduced into the blood by a woun may be swallowed with impunity.

(*e*) *Other less known Bases.*

(1216) The bulbs of the *colchicum autumnale* and t and seeds of different species of *Veratrum* contain several a the most important of which, *veratria,* has been employe cinally. Veratria ($C_{64}H_{52}N_2O_{16}$; Merck) occurs principally i nation with gallic acid; it is an extremely acrid and violent producing dangerous fits of sneezing if it come in contact, minute quantity, with the mucous membrane of the nose. as a valuable sedative in some cases of neuralgia if applie form of ointment to the surface of the body. Veratria is insoluble in water and in alkaline solutions; alcohol diss freely, and deposits it by spontaneous evaporation, in long needles. Ether dissolves it with difficulty; fuming sulph colours it yellow, then blood-red, and lastly, violet. Nit strikes with it a red which after a time becomes yellow. Three other poisonous bases, *sabadillia*, *colchinia*, and *jervia*, are found, along with veratria, in the *Veratrum album*, or white hellebore. Jervia ($C_{60}H_{45}N_2O_5+4$ Aq) is white, crystalline, and fusible.

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* Schutzenberger (*Ann. de Chimie,* III. liv. 65) states that h the base reputed to be igasuria, no fewer than nine closely relat which could be separated by fractional crystallization from boili They are all intensely bitter, and are poisonous, resembling strychni effects. They all are reddened by nitric acid; he assigns to them th ing formulæ:—

(*a*) $C_{44}H_{26}N_2O_8 + 6\,Aq$ very sparingly soluble;
(*b*) $C_{36}H_{24}N_2O_{14} + 6\,Aq$ sparingly soluble;
(*c*) $C_{36}H_{24}N_2O_8 + 6\,Aq$ moderately soluble;
(*d*) $C_{34}H_{32}N_2O_{16} + 6\,Aq$ moderately soluble;
(*e*) $C_{36}H_{26}N_2O_8 + 6\,Aq$ soluble;
(*f*) $C_{42}H_{30}N_2O_8 + 6\,Aq$ or 8 Aq: soluble;
(*g*) $C_{42}H_{28}N_2O_{12} + 6\,Aq$ sparingly soluble;
(*h*) $C_{42}H_{26}N_2O_{12} + 6\,Aq$ moderately soluble;
(*i*) $C_{40}H_{26}N_2O_{14} + 6\,Aq$ moderately soluble.

These results afford an illustration of the vast number of bases whic produced by the actions of a single plant; they show the difficulty i gations of this kind, and may serve to explain the discordant results sometimes arrived at by chemists of tried ability.

Aconitina ($C_{60}H_{47}NO_{14}$?) is another intensely poisonous alkaloid, which is employed medicinally, but the composition of which is uncertain; it is obtained from various species of monkshood or aconite. It crystallizes with difficulty, and is more soluble in water than most of these bases; it is dissolved easily by alcohol and ether. These solutions have a powerfully alkaline reaction; and the base forms perfectly neutral salts, which when moistened with concentrated sulphuric acid acquire a colour which at first is yellowish, and then becomes of a dirty violet red.

Many of the *Solanaceæ* and *Umbelliferæ* contain alkaloids. The henbane (*Hyoscyamus niger*) and both the common and the deadly nightshade (*Solanum dulcamara*, and *Atropa belladonna*) owe their poisonous qualities to compounds of this kind. To *Solania* Zwenger assigns the formula $C_{86}H_{70}NO_{32}$.

Atropia ($C_{34}H_{23}NO_6$; Planta) crystallizes in colourless silky needles, which are freely soluble in alcohol and in chloroform, but less so in ether. The crystals fuse at 194°, and undergo sublimation and partial decomposition at 284°. Solutions of atropia are speedily altered by evaporation when exposed to the atmosphere. Atropia is present in all parts of the belladonna, but is commonly extracted from the root. It appears to be identical with *daturia*, the active principle contained in the seeds of the *Datura stramonium*. The salts of atropia are bitter, acrid, and highly poisonous, producing a remarkable dilatation of the pupil of the eye.

In addition to these bases two others may be mentioned, viz., *harmaline* and *harmine*, which are found, probably combined with phosphoric acid, in the husk of the seeds of the *Peganum harmala*, or Syrian rue, a plant extensively grown in the steppes of Southern Russia. The seeds of this plant are used in dyeing silk, to which they impart various shades of pink, rose, or red. The seeds also possess narcotic properties, but the active principle to which this effect is due has not been investigated. *Harmaline* ($C_{26}H_{14}N_2O_2$) when pure crystallizes in colourless prisms, but they generally retain a brownish yellow tint, and tinge the saliva yellow. It has a bitter, astringent, acrid taste; it is freely soluble in alcohol, but sparingly so in water and in ether. It is fusible and volatile; with acids it forms yellow, very soluble, crystallizable salts. Oxidizing agents transform it into a red colouring matter which combines with acids, forming salts which constitute the basis of the *harmala red* of commerce. Harmaline contains two atoms more of hydrogen than *harmine* ($C_{26}H_{12}N_2O_2$), into which it may be converted by oxidation: harmine crystallizes in long delicate prisms; it forms colourless salts, which are quite neutral.

Emetia, the active principle of ipecacuanha, also possesses the properties of a feeble base: it is nearly insoluble in water and in ether, but is readily soluble in alcohol and in dilute acids; chloroform also dissolves it with facility. It is a powerful poison, and acts as a violent emetic in doses of the one-sixteenth of a grain or less. It fuses readily, and is accompanied in the ipecacuanha root by a large proportion of oily matter, which emits a feeble odour of tobacco when heated. The base is easily obtained by treating the alcoholic extract of the root with dilute sulphuric acid, filtering from the oily matter, and after slightly supersaturating the solution with ammonia, agitating the turbid liquid with chloroform. On evaporating the chloroform, the emetia is left as a yellowish resinous-looking mass. It may be purified by conversion into a salt, and digesting its solution with a small quantity of animal charcoal; on adding an alkali to the filtered liquid the emetia is precipitated. The salts of emetia do not readily crystallize.

(*f*) *Alkaloids of Coffee, Tea, and Chocolate.*

(1217) CAFFEINE OR THEINE ($C_{16}H_{10}N_4O_4+2Aq=194+18$).—This substance occurs in tea, in coffee, and in *maté*, a shrub used by the natives of Paraguay and a large number of the inhabitants of South America, for making an infusion which they substitute for tea. It is also contained to the extent of 5 per cent. (Stenhouse) in *guarana*, an astringent species of chocolate prepared from the fruit of the *Paullinia sorbilis*. Tea appears to contain from 2 to 4 per cent. of caffeine (Péligot), but the quantity of it in coffee, according to Stenhouse, seldom exceeds 1 per cent.

Caffeine is easily obtained from tea by making a strong infusion of the leaf, mixing it with subacetate of lead and a little free ammonia, to separate tannic acid, and transmitting sulphuretted hydrogen to remove the excess of lead; on then evaporating the solution and allowing it to cool, the caffeine crystallizes out in long flexible silky needles.

It has a slightly bitter taste, and is sparingly soluble in cold water and in alcohol; both boiling water and ether dissolve it in considerable quantity. The crystals deposited from alcohol and from ether are anhydrous. Caffeine fuses at 454° (Strecker), and at a higher temperature it may be sublimed without decomposition.

The basic properties of caffeine are only slightly marked, but it forms crystallizable salts with hydrochloric and sulphuric acids; both these compounds are, however, decomposed by solution in water. Caffeine absorbs about a third of its weight of dry hydrochloric acid gas; the compound must be crystallized from a concentrated solution of hydrochloric acid, and the crystals washed with ether. Caffeine forms with nitrate of silver a crystalline compound ($C_{16}H_{10}N_4O_4+AgO,NO_5$) which may be recrystallized from boiling water or from alcohol; it is sparingly soluble in cold water.

Wurtz found that when caffeine is boiled with potash, methylia is liberated. Concentrated nitric acid decomposes caffeine with evolution of nitrous fumes, and the formation of a yellow liquid, in which at a particular stage the addition of ammonia developes a beautiful purple colour, resembling that of murexid; by longer boiling the decomposition proceeds further, salts of methylia are found in solution, and cholestrophan is formed. Similar results are furnished by the action of chlorine. The purple reaction is most easily obtained by treating the caffeine with a mixture of hydrochloric acid and chlorate of potash, evaporating to dryness, and then adding a little ammonia.

When chlorine is transmitted through a magma of caffeine suspended in water, the crystals gradually disappear, and a mixture of several products is obtained; of these the most remarkable are *amalic acid* ($C_{12}H_7N_2O_8$), and *nitro-theine* or *cholestrophan* ($C_{10}H_6N_2O_6$), whilst a salt of methylia is formed. By evaporating the solution, amalic acid may be obtained in colourless crystals, which are insoluble in alcohol; they assume a violet colour if moistened with baryta water. Cholestrophan may be obtained in pearly scales on evaporating the solution; it may be sublimed unaltered. According to the researches of Rochleder (Liebig's *Annal.*, lxxiii. 123), the products of the oxidation of caffeine resemble those obtained from uric acid by similar treatment, and the two classes of compounds are homologous, or rather substitution products from the same organic group; for amalic acid corresponds to alloxantin, in which 2 atoms of hydrogen have been displaced by two equivalents of methyl; and cholestrophan bears a similar relation to parabanic acid:—

Alloxantin	$C_8H_3N_2O_8$, 2 $HO=C_8H_5N_2O_{10}$,
Amalic acid (dimethyl-alloxantin)	$C_8H(C_2H_3)_2N_2O_8$,
Parabanic acid	$C_6H_2N_2O_6 \quad = 2\ HO,C_6N_2O_4$,
Cholestrophan (dimethylo-parabanic acid)	$C_6(C_2H_3)_2N_2O_6$.

Strecker, by heating dry parabanate of silver with anhydrous iodide of methyl in a sealed tube, has, indeed, effected its conversion into cholestrophan (methyl parabanic ether) and iodide of silver:—

$$2\ AgO,C_6N_2O_4 + 2\ C_2H_3I = 2\ C_2H_3O,C_6N_2O_4 + 2\ AgI.$$

Amalic acid also possesses the property, like alloxantin, of staining the fingers pink; and if exposed to the vapour of ammonia, it produces a compound homologous with murexid, which, like the latter compound, is distinguished by its magnificent purple colour:—

Murexid	$C_{24}H_{12}N_{10}O_{16}$
Caffeo-murexid	$C_{36}H_{24}N_{10}O_{16}$

In the latter case the difference between the two compounds is $3\ (C_4H_4)$, because murexid is the result of a reaction of ammonia upon three molecules of alloxantin, and caffeo-murexid in like manner is derived from three of amalic acid.

(1218) *Chemical and dietetic characters of Coffee and Tea.*—Caffeine is a compound which presents a high degree of interest both from the metamorphoses of which it is susceptible, and from the circumstance that it forms an ingredient in three substances, namely, tea, coffee, and a third substance of less importance, *maté* (or Paraguay tea, obtained from the *Ilex Paraguayensis*), one or other of which constitutes a portion of the daily diet of three-fourths of the human race. The circumstance that these different shrubs should have been selected by different nations, for the purpose of yielding a beverage, when infused with boiling water, shows that the ingredient which they furnish is one which is adapted in a special manner to some craving of the human frame. Although these bodies differ so widely in flavour, they all contain the same azotised principle, the physiological effects of which have not been submitted to the detailed examination which they well deserve. The best series of experiments upon this point are due to Julius Lehmann, who watched for some weeks the effects of roasted coffee, as well as of its essential oil, and of caffeine, upon two individuals in good health (Liebig's *Annal.*, lxxxvii. 205). The use of coffee as an article of diet appears to exercise an important influence in retarding the waste of the tissues of the body; since it was found that during its use, the proportion of phosphoric acid and of urea excreted by the kidneys, was much smaller than when the coffee was omitted, the diet being in all other respects the same in both cases. Thus, it was found that when an infusion of three-quarters of an ounce of roasted coffee-berries was taken daily for a *fortnight*, the average proportion of urea and of phosphoric acid which passed off by the kidneys in 24 hours, was less by one-third than it was during a similar period in which the coffee was omitted. The empyreumatic oil of the coffee was found to exert a stimulating effect upon the nervous system. When too large a quantity of this essential oil was taken, it produced loss of sleep, nervous excitement, and symptoms of congestion of the brain. In smaller quantities it produced a gentle perspiration, removed the sensation of hunger, and acted upon the bowels as a laxative. It likewise reduced the amount of urea and of phosphoric acid in the urine. It was also concluded from the production of similar alterations in the quality of the urine, when a solution of pure caffeine was substituted for the ordinary infusion of coffee, that caffeine likewise exerted a power of retarding the disintegration of the constituents of the animal frame.

Tea, coffee, and the Paraguay tea-plant, in the form in which they are used dietetically, all contain the following principles:—1. Caffeine. 2. One of the forms of tannic acid. 3. An aromatic essential oil, which is different in each plant, and is the main cause of their different and peculiar flavours.

Constituents of Coffee.—When the coffee berry is first gathered and dried in the air, it has but little fragrance, and only a slightly bitter and astringent taste. The raw coffee berry is hard and horny; it swells up with difficulty even when heated with boiling water; it contains in its green state about the same quantity of soluble matter as after it has been roasted; but the amount varies greatly in different specimens.

Coffee swells considerably during roasting, the increase in volume amounting to one third or even to one half of its original bulk; at the same time it loses in weight to an extent varying from 15 to 25 per cent. upon the weight of the berries before roasting; the amount of this loss depending upon the extent to which the roasting is carried. The roasting should be stopped as soon as the berry has become friable. The agreeable bitter aromatic taste of coffee is developed during this operation. It is worthy of remark that inferior coffee becomes improved in quality by keeping, and if roasted after it has been kept for some years, it yields an infusion of a finer flavour than if roasted immediately after it has been gathered. Both the essential oil and the bitter flavour are developed from one of the soluble constituents of the berry, since the aqueous extract of the raw berry when roasted acquires the full odour and taste of coffee. The proportion of this aromatic oil in roasted coffee is very minute; not exceeding, according to Payen, one five-thousandth of the weight of the coffee. Coffee also contains 14 or 15 per cent. of fixed oil. The astringent acid, *caffeic acid*, as it has been termed, is allied to the quinic; it constitutes about 5 per cent. of the dry berry: it does not blacken the solution of protosulphate of iron, but turns it green, and it does not precipitate solutions of gelatin; it is dissolved by strong sulphuric acid and produces a red liquid. When exposed to the air in contact with alkalies, caffeic acid absorbs oxygen and forms a yellow insoluble resin.[*] A peculiar reaction occurs with caffeic acid when 1 part of its concentrated solution is heated with four parts of finely-powdered black oxide of manganese, and one part of oil of vitriol diluted with an equal bulk of water. Yellow crystals of quinone (1127) are deposited upon the neck and sides of the retort, and the acid liquid which distils over is saturated with quinone, and contains formic acid. (See a Report on the adulterations of coffee by Graham, Stenhouse, and Campbell, *Q. J. Chem. Soc.*, ix. 52.) The acid of Paraguay tea, and that of the leaves of the holly tribe, also furnish quinone by similar treatment. The following is the average composition of the coffee-berry, according to Payen:—

Ligneous tissue	34·0
Hygroscopic water	12·0
Fixed fatty matters	10 to 13·0
Gum, sugar, and a vegetable acid	15·5
Azotised matter, analogous to legumin	13·0
Free caffeine	0·8
Compound of caffeine with potash and chlorogenic (caffeic) acid[†]	3·5 to 5·0
Aromatic essential oil	0·002
Solid fatty essence	0·001
Saline matters	6·697

The saline matters contained in coffee contain more than half their weight of potash (51·5 to 55·8 per cent.) chiefly in the form of carbonate and phosphate; they are almost entirely free from silica. The sugar in raw coffee is in the form of cane sugar (Graham, Stenhouse, and Campbell), and its quantity varies from 6·2 to 7·7 per cent. The process of roasting not only expels the greater part of the hygroscopic moisture, but it considerably ifies the properties of the caffeic acid, and converts nearly the le of the sugar into caramel. The solid portion left after sing the ground berry in water contains a large amount of ritious substance, in the form of an azotised principle resem- g casein or legumin. This may account for the practice among Arabs and other oriental nations, of swallowing the undissolved ions of the grain with the decoction: in the countries of tral Asia the use of animal food is rare, and hence the inhabit- have been led to vary the mode of preparing their coffee in a manner as to enable them to use the substance in some sure as a substitute for the nitrogenous constituents supplied flesh diet.

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[*] Vlaanderen and Mulder have recently made a minute investigation of the *caffeic acid*, which gives a yellow precipitate with salts of lead, and to which they assign the formula, when anhydrous, of $C_{14}H_8O_7$. A second acid termed *caffelic acid* $C_{14}H_8O_{12}$, gives a white precipitate with salts of lead.

[†] Containing 39 per cent. of caffeine; 3·5 parts, therefore, indicate 1·36 of caffeine. This salt has not been found by other chemists.

The dried leaves of the coffee-plant also contain as much as per cent. of caffeine (Stenhouse), as well as an astringent vege- acid, and a large proportion (13 per cent.) of an azotised prin- allied to gluten. The dried coffee-leaf has an agreeable ; it is used largely in the form of infusion by the natives of tra, who prefer it as a beverage to that prepared from the berry.

Constituents of the Tea-plant.—The dried leaves of the *Thea nsis*, which constitute our ordinary 'tea,' contain about 45 cent. of soluble matter; but, according to Péligot, tea does not ally give up more than about one-third of its weight of soluble tter to boiling water. The most important constituents of the in the form in which it is consumed in Europe, are:—1. *The ntial oil*, to which it owes its peculiar aroma, and the pro- ion of which, according to Mulder, is about 0·79 in green, and per cent. in black tea. This oil exerts a most powerfully ulating and intoxicating effect. In China, tea is seldom used it is a year old, on account of the well-known intoxicating s of new tea, due probably to the larger proportion of essen- oil contained in the freshly dried leaf. 2. *Caffeine*, or theine, quantity of which varies considerably in different varieties of in different kinds of green tea furnished to Péligot, the nts ranging from 2·2 to 4·1 per cent. 3. A *nitrogenized com- d* analogous to casein, amounting to 14 or 15 per cent. of weight of the leaf. Almost the whole of this material is n away in the spent leaves, which when dry contain not less 18 per cent. of their weight of this substance.* 4. *The*

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he Mongol Tartars economize a large portion of this nutritive matter ng the powdered tea with the alkaline water of their steppes, to which ity of salt is added; by this means a notable proportion of the gluten is d or suspended in the liquid, which they commonly eat thickened with , milk, and baked flour (Lehmann).

astringent principle, which is a modification of tannin; it
a precipitate in solutions of gelatin, and produces a bl
protosulphate of iron: it constitutes from 13 to 18 pe
the dried leaf. The ash of tea varies from 5·3 to 5·6 per c
dried leaf; a portion of this ash is probably due to the
matter which the Chinese are in the habit of adding to t
teas, for the foreign market; this colouring matter is in s
indigo, in others a mixture of Prussian blue and pipe-cla

It appears from the observations of Mr. Fortune, th
green or black tea can be obtained at pleasure from
plant. *Green tea* is prepared from the young leave
within an hour or two after they have been gathered, a
in pans over a brisk wood fire. After four or five minute
the leaves become flaccid, and are rolled by the hand
wooden table; they are then again thrown into the dr
where they are kept in rapid motion, and in about an ho
hour and a half, are completely dried.

Black tea is allowed to lie in heaps for ten or twelve h
the leaves have been gathered; they are then tossed abou
time till they become flaccid. At this stage they begin
fragrant smell; they are next rolled in balls, with the h
a wooden table, and a large quantity of liquid is expre
them, after which they are shaken out, roasted for a few
again rolled; and, whilst still flaccid, are exposed to th
some hours upon shallow bamboo trays: this alternat
and rolling is repeated three or four times; and, fi
leaves are dried slowly over charcoal fires. A species of f
tion appears to occur during the drying of the leaf, i
quence of which a development of essential oil takes
which the agreeable aroma is occasioned: this aroma is
in the fresh leaf. The change of the leaf from green
is mainly due to chemical alterations produced by the
of the air upon the constituents of the leaf, and especi
the astringent principle; this change being prevented in
by the rapid process of drying to which it is subjected.

(1219) *Theobromine* ($C_{14}H_8N_4O_4$; Glasson).—This
present in chocolate. It is extracted from the cacao-nu
broma cacao) by a process similar to that employed in
caffeine from tea or coffee. Theobromine is but sparingly
in boiling water, and still less so in alcohol and in ether;
slightly bitter taste. At a high temperature it may be s
a part of it undergoing decomposition during the proc
resembles caffeine in its property of forming crystalliza

ne of the acids; but these compounds are decomposed by nd its basic powers are very feeble.

obromine when dissolved in ammonia, and mixed with of silver, yields a gelatinous precipitate, which, by boiling olution of ammonia, becomes converted into a crystalline f this be dried and heated in a sealed tube with anhydrous f methyl, iodide of silver is formed, and caffeine is pro- Strecker) :—

$$\overbrace{C_{14}H_7AgN_4O_4}^{\text{Theobromide silver.}}+\overbrace{C_2H_3I}^{\text{Iodide methyl.}}=\overbrace{C_{16}H_{10}N_4O_4}^{\text{Caffeine.}}+2\,AgI.$$

is, therefore, a methyl-compound of theobromine, and not omologue of it, as its formula might seem to indicate.

cacao-nut is remarkable for the large proportion of fatty which it furnishes. This fat is not liable to become rancid, nstance which adds greatly to the value of the nut as an of food. The nut, when deprived of its husk, is said in nearly 56 per cent. of this fat, 17 per cent. of a sub- resembling gluten, from 1·2 to 1·5 of theobromine, and 22 h, gum, sugar, and ligneous tissue. The aromatic flavour a is due to the roasting to which the nut is subjected s to grinding it. If the roasted nut be simply crushed has been freed from its husk, it forms the *cocoa nibs* of cer. *Chocolate* is prepared by grinding the roasted nut aste between hot rollers, and mixing it with sugar, vanilla, on and other spices.

number of well-defined bases of animal origin is but small, they are generally produced by the decomposition of azotised nds not as yet described, it will be more convenient to eir consideration till a later period. (1411 *et seq.*)

II. GENERAL REVIEW OF THE MONATOMIC ALCOHOLS ($C_{2n}H_{2n+2}O_2$).

20) Having now completed the description of the more nt bodies connected with the alcohols of the form $_{2}O_2$), it may be serviceable to take a general review of the on of these different compounds with each other. For pose the following table has been constructed; it furnishes tic view of the more important classes of heterologous ves from these alcohols :—

Heterologous Series derived from the Alcoh

	Name of the Series	and General Formula.	Exa
1.	Electro-positive radicle	$(C_{2n}H_{2n+1})_2$	Ethyl
2.	Double radicle	$(C_{2n}H_{2n+1}, C_{2m}H_{2m+1})$	Ethyl-tetryl
3.	Alcohol	$(C_{2n}H_{2n+1}, H)O_2$	Alcohol
4.	Simple ether	$(C_{2n}H_{2n+1})_2O_2$	Ethylic ether
5.	Double ether	$(C_{2n}H_{2n+1}, C_{2m}H_{2m+1})O_2$	Ethyl-amylic ether
6.	Hydracid ether	$(C_{2n}H_{2n+1})\overline{W}$	Hydrochloric ether
7.	Sulphuretted ether	$(C_{2n}H_{2n+1})_2S_2$	Hydrosulphuric ether
8.	Bisulphuretted ether	$(C_{2n}H_{2n+1})_2S_4$	Bisulphide of ethyl
9.	Mercaptan	$(C_{2n}H_{2n+1}H)S_2$	Ethyl-mercaptan
10.	Compound ether (monobasic)	$(C_{2n}H_{2n+1})O, \overline{X}$	Acetic ether
11.	Compound ether (dibasic	$(C_{2n}H_{2n+1})_2O_2, \overline{Y}$	Oxalic ether
12.	Vinic acid	$HO, (C_{2n}H_{2n+1})O, \overline{Y}$	Sulphethylic acid
13.	Salt of vinic acid	$MO, (C_{2n}H_{2n+1})O, \overline{Y}$	Sulphethylate of potash
14.	Compound ether (tribasic)	$(C_{2n}H_{2n+1})_3O_3, \overline{Z}$	Citric ether
15.	Cyanide, or nitrile	$(C_{2n}H_{2n+1})Cy$	Hydrocyanic ether (propio-nitrile)
16.	Amide bases	$H_2(C_{2n}H_{2n+1})N$	Ethylia
17.	Imide bases	$H, (C_{2n}H_{2n+1})_2N$	Diethylia
18.	Nitrile bases	$(C_{2n}H_{2n+1})_3N$	Triethylia
19.	Oxide of ammonium base (hydrated)	$(C_{2n}H_{2n+1})_4NO, HO$	Oxide of tetrethylium (hydrated)
20.	Homologues of urea	$H_3(C_{2n}H_{2n+1})N_2C_2O_2$	Ethyl-urea
21.	Zinc-radicle	$[Zn(C_{2n}H_{2n+1})]_2$	Zinc-ethyl
22.	Diarsenio-radicle	$As(C_{2n}H_{2n+1})_2$	Kakodyl
23.	Oxide of diarsenio-radicle	$As(C_{2n}H_{2n+1})_2O$	Oxide of kakodyl
24.	Acid of diarsenio-radicle	$HO, As(C_{2n}H_{2n+1})_2O_3$	Kakodylic acid
25.	Triarsenio-radicle	$As(C_{2n}H_{2n+1})_3$	Triarsenethyl
26.	Oxide of triarsenio-radicle	$As(C_{2n}H_{2n+1})_3O_3$	Oxide of triarsenethyl
27.	Hydrated oxide of tetrarsenio-radicle	$As(C_{2n}H_{2n+1})_4O, HO$	Hydrated oxide of tetrarsenethylium
28.	Stanno-radicles	$XSn(C_{2n}H_{2n+1})x$	Distannethyl
29.	Homologues of marsh gas	$(C_{2n}H_{2n+1})H$	Hydride of ethyl
30.	Homologues of olefiant gas	$(C_{2n}H_{2n-1})H$	Olefiant gas
31.	Homologues of acetylene	$C_{2n}H_{2n-2}$	Acetylene
32.	Aldehyds	$(C_{2n}H_{2n-1})H, O_2$	Acetic aldehyd
33.	Volatile acids	$HO, (C_{2n}H_{2n-1})O_3$	Acetic acid
34.	Ketones	$C_{2n}H_{2n}O_2$	Acetone
35.	Dibasic acids	$2\,HO, (C_{2n}H_{2n-4})O_6$	Succinic acid
36.	Monobasic anhydrides	$(C_{2n}H_{2n-1}O_3)_2$	Acetic anhydride
37.	Compound anhydrides	$C_{2n}H_{2n-1}O_3, C_{2m}H_{2p-1}O_3$	Benzo-acetic do.
38.	Dibasic anhydrides	$C_{2n}H_{2n-4}O_6$	Succinic anhydride
39.	Monobasic oxychlorides	$C_{2n}H_{2n-1}O_2Cl$	Acetic oxychloride
40.	Dibasic oxychlorides	$C_{2n}H_{2n-4}O_4Cl_2$	Succinic oxychloride

If space allowed us to map out the whole of the various vatives of each alcohol in a table similar in principle to that n at pages 34 and 35, each of the general formulæ given in second column of the preceding table would stand at the head ne of the columns of such a table. Each substance enumerated is table is, therefore, to be regarded as the representative of a ologous series of compounds like that of the fatty acids, or of lcohols, in which each of the members differs from those h immediately precede and follow it by (C_2H_2).

It will be observed that the letters $\overline{W}$, $\overline{X}$, $\overline{Y}$, and $\overline{Z}$, are occa- lly employed in the column headed "General formulæ":—

$\overline{W}$ indicates chlorine, or one of the halogens.
$\overline{X}$ indicates an anhydrous monobasic acid.
$\overline{Y}$ indicates an anhydrous dibasic acid.
$\overline{Z}$ indicates an anhydrous tribasic acid.

t must be remembered that this table, extensive as it is, not specify all the known heterologous derivatives of any alcohol. The different forms of the phosphorus bases are entioned, because they are represented by the formulæ of e of ammonium, from which they differ in containing an atom hosphorus in the place of one of nitrogen. Of the homologues rea two distinct series are known, the first of which corresponds thyl-urea $[H_3(C_4H_5)N_2C_2O_2]$, and the second to diethyl-urea $(C_4H_5)_2N_2C_2O_2]$, though the former series only is indicated in table. With the exception of the ureas neither amides nor atomic bases appear in the table. The zinc-radicle again repre- ts other metallic compounds, such as those containing cadmium, h are formed upon the same type. The various arsenio-com- ds are also representatives of the antimony series, which are mentioned in the table; the arsenical compounds likewise are entatives of the compounds which contain bismuth in the e of arsenic. Again, the stanno-radicles, themselves a numerous p, are only indicated by a single formula; whilst the compounds d and of mercury correspond to one or other of the different s of the stanno-radicle.

CHAPTER VII.

ESSENTIAL OILS AND RESINS.

§ I. Essential Oils.

(1221) The odoriferous principle of most plants resides in certain compounds consisting chiefly of carbon and hydrogen; and although the boiling point of these bodies lies considerably above 212°, they emit at ordinary temperatures minute quantities of an intensely odorous vapour. They have a certain resemblance to the fixed oils in their inflammability, sparing solubility in water, and ready solubility in alcohol and in ether; as well as in the production of a greasy stain when dropped upon paper, though this mark is only transient; and they feel harsh instead of unctuous when rubbed upon the skin: from the points of their similarity to the oils, and from the fact of their constituting in many cases the distinctive compound of the plant which yields them, they are termed *essential* or *volatile oils*.

The production of the essential oils is not limited to any particular portion of the vegetable organism. In some natural families—as, for instance, in the *Umbelliferæ*,—the oil is most abundantly contained in the seeds. The *Aurantiaceæ* yield two different kinds of essential oil, one of which is obtained from the flower, and the other from the rind of the fruit. The *Myrtaceæ* and the *Labiatæ* supply it from the leaves, whilst the *Rosaceæ* contain it only in the petals of the flower.

Generally speaking, the oils appear to exist ready formed in the plant, being enclosed in little sacculi, which are often visible to the naked eye, as in the leaves of the *Myrtaceæ* and the peel of the *Aurantiaceæ*. In a few cases, such as those of the oils of bitter almonds and of mustard, they are produced by a species of fermentation operating on a principle contained in the cells of the seed; this change does not commence until the seed has been crushed and mixed with water. A peculiar azotised body present in the seed is thus brought into contact under favourable circumstances with the compound which yields the oil, and the peculiar aroma of the essence is speedily developed.

The oils of lemon and orange are extracted by simple pressure of the rind of the fruit; but the general process of extraction consists in placing the appropriate portions of the plant in a still, with water, and applying heat; in order to prevent the vegetable

ls from being over-heated by resting against the sides of the
hich would give to the distillate a disagreeable odour, it is
ary to suspend them in a net or perforated metallic vessel
upper part of the still. A better method of obtaining the
is to allow steam to pass over the plant, and to condense
our afterwards in the usual way. The presence of steam
the volatilization of the oils at a comparatively low
ature, for it mechanically carries over the vapour: the
e is at first milky, but the greater portion of the essence
es from the milky liquid on standing. The water which
ensed in a receiver with the oil acquires the odour and
the essence; such waters constitute the fragrant *distilled*
of the apothecary: by a second distillation, these waters
d from some impurities which are mechanically carried
nd which would cause the liquid to become mouldy, and
its fragrance. A small quantity only of the essential oil is
d in solution in the distilled water, and the greater portion
oil which is thus retained may be separated by saturating
uid with chloride of sodium; the essence on standing rises
surface. It may also be removed by agitating the distilled
with ether, which dissolves the oil; and on expelling the
from the layer which separates on standing, the pure oil is
ed. In some cases, where the essence becomes altered
the act of distillation, the fragrance of the plant is obtained
ncentrated by dissolving it in a fixed oil, which is itself
te of odour, such as oil of poppy-seeds. The leaves of the
are in such instances spread in thin layers upon woollen
saturated with the fixed oil, the cloths thus charged are
iled one upon another, and submitted to the action of a

e essential oils vary in specific gravity, but in general they
hter than water. These oils are usually liquid at ordinary
atures, but oil of aniseed is solid at all temperatures
60°. If cooled slowly, many of them separate into a solid
fluid portion, respectively termed *stearopten* and *elæopten*.
ct is readily explained by the circumstance that most of
ntial oils are mixtures of two or more distinct chemical
nds which differ in volatility and fusibility; one of these
nds generally contains no oxygen, whilst the others are
ubstances formed from it by oxidation. Of these the pure
rbon is generally the more volatile; it acts as a solvent to
lized compounds, which, by a depression of temperature,
quently be separated from it in a crystallized form.

Most of the essential oils have a yellowish colour, which deepens when exposed to the air; during such exposure they absorb oxygen more or less rapidly, and are thus gradually converted into a solid, resinous, or camphreous mass. Those oils which absorb oxygen the most rapidly have in general the most powerful odour. This absorption of oxygen is sometimes attended with a simultaneous extrication of carbonic acid and water: this occurs in the case of the oils of anise, and of lavender; and in such instances the resulting resinous mass is not a simple oxide of the hydrocarbon.

The essential oils are insoluble in potash, and are not capable of saponification by treatment with alkalies: but if the oils be transmitted in the form of vapour over heated hydrate of potash, hydrogen is frequently disengaged, and the oil becomes oxidized, forming an organic acid which enters into combination with the potash. Oil of cinnamon may thus be converted into cinnamate of potash:—

$$\overbrace{C_{18}H_8O_2}^{\text{Oil of cinnamon.}} + KO{,}HO = \overbrace{KO{,}C_{18}H_7O_3}^{\text{Cinnamate of potash.}} + H_2.$$

Chlorine, iodine, and bromine act upon most of the essential oils, and form compounds in which a certain number of atoms of these elements displace a corresponding number of atoms of hydrogen. Nitric acid oxidizes most of the essential oils with great violence.

The essences may be arranged under three principal divisions, viz.—*A.* Pure hydrocarbons; *B.* Oxidized essences: *C.* Sulphuretted essences.

The pure hydrocarbons are generally lighter than water; the other two varieties often have a specific gravity greater than that of water.

The essences which belong to the first class always occur in a state of admixture with a larger or smaller proportion of an oxidized compound.

(*A.*) *Pure Hydrocarbons.*

(1222) The group of chemical compounds formed by the essential oils which contain no oxygen presents many interesting features: sixteen or twenty of these substances are isomeric. These isomeric bodies may be subdivided into two metameric classes; in one of which the molecule is represented by $C_{20}H_{16}$; to which class oil of turpentine belongs; in the other, the molecule of the oil, like that of essence of cubebs, is represented by

The members of each of these groups, notwithstanding ity of their odour and taste, are strictly metameric; ghts yielding exactly equal volumes of vapour. The ese groups, the members of which are termed *terebenes* *gens,* is the more numerous and important. Many cha- oth chemical and physical, are common to all the f the group: for example, they have a specific gravity id form closely approaching to 0·860; and the boiling- igh subject to greater variations, in most instances is 320°.

of the terebenes cannot be distinguished from each other their action upon polarized light: some varieties of oil ine, for example, cause left-handed rotation of a ray of ight; oil of lemons produces rotation to the right hand; er oils are destitute of rotatory action upon the plane of n. A slight change in the molecular arrangement of tuent particles of these bodies modifies their action ized light, for it has been found that oil of turpentine r treatment at a high temperature may be deprived of y power, although it retains its usual chemical pro- 125).

erebenes rapidly absorb dry hydrochloric acid gas, and ounds termed *artificial camphors;* some of these bodies , and in appearance and properties much resemble mphor; while others of the oils form combinations with qually definite, but which retain the liquid form. Oil ine and oil of lemons both form solid compounds with ric acid as well as liquid ones; but the oils of black l of bergamotte form only liquid compounds:—

Artificial camphors.		
m oil of turpentine .	solid	$C_{20}H_{16}$, HCl
m oil of lemons . .		$C_{20}H_{16}$, 2 HCl
m oil of black pepper	liquid	5 ($C_{20}H_{16}$) 8 HCl
m oil of bergamotte .		3 ($C_{20}H_{18}$) HCl,HO.

gous compounds with the other hydracids, such as the ic and the hydriodic, may also be obtained.

er remarkable feature of the terebenes is the power y possess of combining with water, and thus forming ile crystalline substances which have a still closer analogy r, both in composition and properties, than the hydro- mpounds. Mere contact of the oil with water, or with ghtly acidulated with nitric acid, in most instances gives rise to these compounds; oil of turpentine furnishing not fewer than three such hydrates, viz.; *terpine* ($C_{20}H_{16}$, 4 HO + 2 Aq); ($C_{20}H_{16}$, 4 HO); and *terpinol*, ($C_{20}H_{16}$,HO); the first two are solid, the last is liquid. Oil of lemons gives two such compounds, viz.: ($C_{20}H_{16}$, 6 HO) and ($C_{20}H_{16}$, 4 HO); and oil of juniper one such hydrate ($C_{20}H_{16}$, 4 HO): the camphor of the *Dryobalanops camphora*, or Borneo camphor, consists of $C_{20}H_{16}$, 2 HO.

All these varieties of camphor when distilled with phosphoric anhydride, lose their water, and yield hydrocarbons, having the composition $C_{20}H_{16}$; ordinary camphor $C_{20}H_{16}O_2$, when similarly treated, also gives a hydrocarbon termed cymol ($C_{20}H_{14}$). Indeed, the simple act of sublimation deprives the camphor or solid hydrate ($C_{20}H_{16}$, 6 HO) of the oils of turpentine, and of lemon, of two atoms of water; the sublimed camphor in each case being represented by the formula, $C_{20}H_{16}$, 4 HO.

The terebenes when exposed to the air absorb oxygen; they become brown and viscid; and are ultimately converted into resins. In many instances this oxidation may be regarded as a simple substitution of oxygen for hydrogen, the number of equivalents of oxygen absorbed corresponding exactly to the number of equivalents of hydrogen removed in the form of water; but in other cases this constitutes only the first stage of the process, and an additional quantity of oxygen combines with the newly formed oxide: a good example of the latter mode of oxidation is seen in the conversion of the liquid oil of lemons into the solid:—

$$C_{20}H_{10}H_6 + 4\ O_4 = C_{20}H_{10}O_6,O_4, + 3\ H_2O_2.$$

(1223) OIL OF TURPENTINE ($C_{20}H_{16}$): *Sp. gr. of liquid* 0·864; *of vapour* 4·76.—Various species of pine, when wounded, pour out a semi-solid resin, of which there are different varieties: that obtained from the *Pinus abies* constitutes *common turpentine*; that from the larch is known as *Venice turpentine*; and that from the *Pistacia lentiscus* forms *Chian turpentine*.

If the turpentine of the *Pinus abies*, or of the *Pinus sylvestris*, be distilled with water, it yields nearly one fourth of its weight of essential oil: this oil passes over with the vapour of water as a volatile, limpid, very inflammable liquid, of a penetrating well-known balsamic odour. The residue in the retort constitutes common *rosin* or *colophony*. Oil of turpentine boils at 320°, and may be distilled unchanged. It mixes freely with alcohol and ether, but not with water; it dissolves the fixed and essential oils, and is largely used in the preparation of many kinds of varnish, since it readily dissolves the resins, and on volatilizing leaves them nd in the form of a transparent coating upon the surface he objects to which it had been applied. Oil of turpentine olves sulphur and phosphorus with facility; it is also one he best solvents for caoutchouc. Most of the *camphine* sold ngland produces a right-handed rotation, and is said to be ished by the *Pinus australis* of the southern States of North rica.

ommercial oil of turpentine frequently consists of a mixture veral isomeric hydrocarbons, which act differently on polarized . The rotation occasioned by Bordeaux turpentine, which is uced chiefly from the *Pinus maritima,* is left-handed, but the unt of the rotation varies in different samples, according to proportion in which the oils are mingled. According to helot, if the ordinary Bordeaux turpentine be distilled *in* o, after saturating the acids which it contains, a homogeneous ocarbon, *terebenthene* (*Sp. gr.* 0·864, *at* 59°), is obtained. It between 318° and 325°. It is endowed with left-handed ary action upon a polarized ray to a definite extent.

(1224) *Modifications of Oil of Turpentine.*—Deville (*Ann. de mie*, II. lxxv. 37, and III. xxvii. 80) and Berthelot (*Ib.*, III. iii. 5) have carefully studied the modifications of which oil of entine is susceptible without undergoing any change in the portion of its components. Some of these modifications retain ir rotatory power upon polarized light, whilst others are inactive this respect:—

a. Active Modifications.—When English essence of turpentine imply heated in a closed vessel to 460° or 480°, it becomes verted into a mixture of several compounds, which boil at erent temperatures; two of these, *isoterebenthene* and *metatere-thene*, may be separated from each other by fractionated distil-on. These modifications may be produced at a lower tempe-re if the essence be heated with water, or with the chloride of ium, of strontium, of zinc, or of ammonium. Fluoride of on, as well as many organic acids, such as the acetic, oxalic, tartaric, also produces similar effects.

1. *Isoterebenthene* (*Sp. gr.* 0·843, *at* 71°; *Boiling pt.* about).—This is a colourless liquid having an odour of stale lemons. xerts a left-handed rotation upon polarized light, but the in- of this power appears to vary with the duration and y of the heat to which it has been exposed. It may be o yield a crystalline hydrate and a solid hydrochlorate.

Metaterebenthene (*Sp. gr.* 0·913, *at* 68°).—This body forms one third of the entire quantity of the essence submitted to heat; it constitutes the residue left in the retort after all the matters volatile below 660° have been expelled. It may be volatilized without decomposition at a temperature somewhat beyond this. It is a viscous yellowish body, possessed of a strong disagreeable odour, and a tendency to rapid oxidation. It exerts a left-handed rotatory power upon polarized light.

Intermediate between these two bodies are other isomeric compounds, of intermediate boiling points; but they have not been specially examined.

b. Inactive Modifications.—Besides these modifications which retain their rotatory power, four other forms of the essence have been procured, which exert no action upon polarized light. These substances are:—

1. Terebene
2. Colophene
3. Camphilene or dadyl
4. Terebilene or peucyl.

The first two have been obtained by acting upon oil of turpentine with sulphuric acid; the last two by decomposing artificial camphor by means of quicklime (1225).

In order to procure terebene and colophene, Deville mixes oil of turpentine with about $\frac{1}{20}$th of its weight of oil of vitriol, in a flask which is artificially cooled. After brisk agitation, the mixture becomes viscous and of a dark-red colour. It must be left at rest for twenty-four hours, during which time it separates into two layers, the lower one being nearly black and strongly acid. The clear liquid is then to be decanted and gently heated: bubbles of sulphurous acid escape, and the colour gradually disappears, whilst the liquid becomes converted into a mixture of terebene and colophene. Upon subjecting the mixture to distillation, terebene passes over in the first portions, and when rectified from a fresh portion of oil of vitriol, is obtained in a state of purity. The last portions of the distillate consist of colophene.

Terebene has a characteristic odour, resembling that of oil of thyme. It boils at the same temperature as the unmodified essence of turpentine, yielding a vapour of the same density, but it is less prone to oxidation. It combines with hydrochloric acid, and forms a liquid compound, $(C_{20}H_{16})_2\,HCl$.

Colophene (*Sp. gr. of liquid* 0·940: *Boiling pt.* from 590° to 600°) yields a vapour, the density of which is twice as great as that of terebene, with which it is polymeric. It absorbs hydrochloric acid, and forms with it a compound of the colour of indigo. In order to obtain colophene in a state of purity, it must be rectian alloy of potassium and antimony (713). Colophene be produced by the distillation of colophony, from which its name. When viewed by direct light it is colourless, hibits the fluorescent character in so marked a degree, rticular directions it appears of a deep indigo-blue. It viscous.

) *Artificial Camphors, and Oils obtained from them.*—It ly been stated that essence of turpentine combines with ric acid, with which it may be made to form two com- $_{20}H_{16},2$ HCl; and $C_{20}H_{16},HCl$.

irst of these bodies may be obtained by allowing the turpentine to remain for some weeks in contact with an a concentrated solution of hydrochloric acid. It forms rectangular prisms, which have an aromatic odour re- that of oil of thyme. It is fusible at 111°, and is ed by distillation.

econd compound ($C_{20}H_{16},HCl$) is obtained by transmitting chloric acid gas into the artificially cooled essence of so long as it is absorbed. As soon as this absorption e compound must be submitted to the action of a freezing f snow and salt, by which it is separated into two por- of which crystallizes, whilst the other remains liquid, F. The production of the liquid compound is favoured on of temperature; if the temperature of the essence be 212° during the absorption of the hydrochloric acid, the npound only is formed. Both the solid and the liquid re found, on analysis, to possess the same composition Cl). The solid body has been termed *hydrochlorate of* or *of dadyl.* It crystallizes in white prisms, which have tic smell and taste, resembling that of ordinary camphor. luble in water; alcohol dissolves one third of its weight his artificial camphor melts at 239°, and boils at 329°, at time undergoing partial decomposition.

hene, Camphilene, or *Dadyl.*—If the vapour of the foregoing pound with hydrochloric acid be transmitted over heated , it is decomposed, chloride of calcium and water are formed, termed *camphilene* (Deville), having the composition of oil tine, is liberated; this body may again be combined with ric acid, in which case the solid artificial camphor is repro- Camphilene boils at 273°. It is entirely devoid of the rotation upon a ray of polarized light.

liquid hydrochlorate has been termed *hydrochlorate of* t is somewhat viscous, and has a sp. gr. of 1·017. If it be distilled with quicklime, *terebilene* (Deville), another hydrocarbon isomeric with essence of turpentine, comes over; it possesses no rotatory power upon polarized light. When again combined with hydrochloric acid, it furnishes a liquid uncrystallizable compound.

Oil of turpentine is not the only one of these essential oils or hydrocarbons which exhibits this remarkable facility of assuming different isomeric states under the influence of heat and of acids. Oil of lemons produces an analogous, though different series of modified products, and most probably the greater number of the essential oils, which are isomeric with oil of turpentine, would be found to furnish like results when subjected to similar treatment.

Hydrates of Oil of Turpentine.—Mention has been already made (1222) of the power which oil of turpentine possesses of slowly combining with water, and forming crystalline compounds. One of these, *terpine* ($C_{20}H_{16}$, 6 HO) may be obtained in the form of rhomboidal prisms, by agitating together frequently, for two or three days, a mixture of 4 measures of oil of turpentine, 1 of nitric acid (sp. gr. 1·36), and 3 of alcohol (sp. gr. 0·840). In the course of a month or six weeks, especially if it be exposed to the sun's rays, voluminous crystals are formed. This hydrate is soluble in 22 parts of boiling water, from which it crystallizes on cooling. It is also freely soluble in alcohol, ether, oil of turpentine, and acetic acid. When sublimed it loses 2 HO, and is converted into the hydrate with 4 HO.

The hydrate ($C_{20}H_{16}$,4 HO) may also be procured when oil of turpentine and water are brought into contact, especially if the temperature be maintained at about 120°: the crystals of this substance fuse at 302°, and boil at 482°. It may be sublimed without being decomposed, and yields a vapour of the sp. gr. 6·257. When exposed to the air it absorbs water, and becomes reconverted into the hydrate with 6 HO.

A third hydrate, termed *terpinol* ($C_{20}H_{16}$,HO, *Sp. gr.* 0·852; *Boiling pt.* 334°), which is liquid at ordinary temperatures, may be obtained by dissolving either of the preceding hydrates in boiling water, adding a little hydrochloric or sulphuric acid, and distilling. Terpinol passes over as an oily liquid, with an odour like that of hyacinths.

(1226) *Products of the Oxidation of Oil of Turpentine.*—Besides the resins which are formed by the spontaneous oxidation of essence of tupentine, various compounds may be obtained from it by artificial processes of oxidation.

When the essence is distilled with bichromate of potash and sulphuric acid, formic acid is produced abundantly. If it be distilled with water and chloride of lime, a copious extrication of carbonic acid takes place with tumultuous violence, and chloroform is found in the products of the distillation. Chlorine acts violently upon oil of turpentine, the reaction being often attended with sufficient heat to inflame the mixture.

If oil of turpentine be heated gently with oxide of lead, it absorbs oxygen rapidly, and becomes converted into formic and *teretinic* acids, which enter into combination with the oxide of lead :—

$$2\,\overbrace{C_{20}H_{16}}^{\text{Oil of Turp.}} + 7\,O_4 = \overbrace{2\,C_{18}H_{14}O_{10}}^{\text{Teretinic acid.}} + 2\,\overbrace{(HO,C_2HO_3)}^{\text{Formic acid.}}.$$

Teretinic acid is soluble in alcohol, from which it may be obtained crystallized in tufts of delicate colourless needles : it is insoluble in water. Most of the compounds of this acid with the metallic oxides are insoluble in water, but soluble in alcohol.

If a few teaspoonfuls of essence of turpentine be introduced into a jar nearly filled with oxygen gas, standing over water, and exposed to the rays of the sun, the interior of the jar speedily becomes coated with brilliant crystals of *hydrated oxide of turpentine* ($C_{20}H_{16},O_2,2\ HO$). This substance may be dissolved in alcohol, from which it may be obtained in crystals. It is also soluble in ether and in boiling water.

Nitric acid acts violently upon oil of turpentine; the two liquids must, therefore, be mixed very cautiously. As the result of the action, a yellow resin is formed, and a quantity of oxalic and terebic acid (1291), besides three other acids, one of which is fusible and may be sublimed; it is termed *terebenzic acid* ($HO, C_{14}H_6O_3$). The second is isomeric with phthalic acid, and is hence termed *terephthalic acid* ($HO,C_8H_2O_3$); it is insoluble in water, alcohol, and ether. The third is termed *terechrysic acid* ($HO, C_6H_3O_4$) in allusion to its yellow colour; it is very soluble in water, and is not susceptible of crystallization.

(1227) *Other Essences which yield Oils isomeric with Oil of Turpentine.*—The following are some of the principal essences which are metameric or isomeric with oil of turpentine :—

Oil of Bergamotte (*Sp. gr.* 0·869), which is obtained from the rind of the ripe fruit of the bergamotte or lime, consists of two portions, viz., a hydrocarbon ($C_{20}H_{16}$), and a solid substance ($C_{30}H_{10}O_{10}$), which may be supposed to be formed from the liquid essence by oxidation ; $3\ C_{20}H_{16} + 12\ O_4 = 2\ C_{30}H_{10}O_{10} + 14\ H_2O_2$.

2. *Oil of Lemons* also contains a solid oxidized essence in small quantity ($C_{20}H_{10}O_{10}$), but the bulk of the oil consists of a hydro-

carbon ($C_{20}H_{16}$), which may be obtained in a state of puri distilling the crude essence. This hydrocarbon is susceptib variety of modifications, analogous to those which may be pr in oil of turpentine. The essential oil from the rind of the appears to be identical with the essence of lemons.

3. *Oil of Neroli* is the fragrant oil obtained from the bl of the orange tree. It is colourless when recently distille becomes red by exposure to light, or by admixture with sul acid. This oil also consists of a hydrocarbon $C_{20}H_{16}$, and oxidized portion which is solid and destitute of odour, the fra of the oil being due to the hydrocarbon.

4. The oil of the *common birch*, which is used in the pr tion of Russia leather, to which it imparts its agreeable od obtained from the tar furnished by the imperfect combust the bark of the tree. It consists of a mixture of sever amongst which the principal is the hydrocarbon $C_{20}H_{16}$, may be isolated by repeated fractionated distillation.

5. *Essence of Camomile :* of this there are two varietie of which is obtained from the *Anthemis nobilis ;* it is of a gr colour, and consists of a hydrocarbon ($C_{20}H_{16}$), and an o portion ($C_{10}H_8O_2$?), which when heated with hydrate of po converted into angelate of potash ($KO,C_{10}H_7O_3$), with evolu hydrogen (1125). The second variety is obtained from th *tricaria chamomilla.* It is remarkable for its deep blue c it contains an oxidized oil ($C_{20}H_{16}O_2$), which has the comp of laurel camphor. It may be distilled without change, mains liquid below 32°.

The oil of the *Achillea millefolium* is also distinguished beautiful blue colour, but it has not been minutely examin

6. *Essence of Juniper* boils at 320°. It produces left- rotation on a ray of polarized light, and if left in contact wit gradually deposits a white crystalline hydrate ($C_{20}H_{16}$,2 HO

(1228) 7. *Oil of Caraway* (*Sp. gr.* 0·938) is obtaine the seeds of the *Carum carvi ;* it consists of two portion hydrocarbon ($C_{20}H_{16}$) has been termed *carvene ;* the oxidiz tion is known as *carvol.* Carvene is a very fluid, colourl lighter than water, with a slight agreeable odour and an taste ; it absorbs hydrochloric acid gas, and forms with it tallizable solid which melts at 123°. Carvol, $C_{20}H_{14}O_2$, is of sp. gr. 0·953 ; it boils at about 437° (Voelckel) : it is with thymol and with cuminic alcohol. Carvol yields camphor ($C_{20}H_{14}O_2$,HCl) with hydrochloric acid. With sulph hydrogen carvol yields a compound termed *hydrosulphate o*

O_2,HS) : this substance is obtained by agitating the less portion of oil of caraway with an equal bulk of alcohol saturated with ammonia and sulphuretted hydrogen ; it is ed in yellowish crystals, which may be recrystallized from alcohol ; they may be volatilized without decomposition. compound be agitated with an alcoholic solution of potash ecomposed, pure carvol is liberated and dissolved by the and on the addition of water it rises to the surface in the an oily layer.

29) 8. *Oil of Cloves* (*Sp. gr.* 1·055 – 1·060).—The berries of ento and the unexpanded flower-buds of the *Caryophyllus cus,* or 'cloves,' yield an essential oil which is not solidified ld of 0° F. It consists chiefly of a hydrocarbon isomeric of turpentine, holding in solution an acid body termed *acid* ($C_{20}H_{12}O_4$). This acid forms a colourless liquid of 1·079 ; that of its vapour is 6·5 ; it emits the odour of oil s : it boils at 469° (Ettling), and forms crystallizable salts e alkalies. Two crystallizable substances are also obtained l of cloves ; one of them is named *eugenin,* and is said to eric with eugenic acid. The other, termed *caryophyllin*)$_2$, is isomeric with ordinary camphor ; it is gradually de- from the oil in crystalline needles.

Oil of Ginger (*Sp. gr.* 0·893) is yellow, and intensely burn- aromatic. It boils at about 475°. It appears to have position of a hydrate of a hydrocarbon isomeric with oil of ine, 4 ($C_{20}H_{16}$)5 HO.

30) 10. *Oil of Cubebs* (*Sp. gr.* 0·929).—When cubebs *cubeba*) are distilled with water, they furnish an essence is colourless and somewhat viscous ; it has a camphreous, ic taste. It boils at a little below 500°, and when distilled a hydrocarbon which furnishes a crystalline compound with hloric acid, consisting of ($C_{30}H_{24}$,2 HCl). This substance t 268°. When essence of cubebs is re-distilled with water, sits a species of camphor ($C_{30}H_{24}$,2 HO), which melts at nd may be distilled at 302° without decomposition. The of cubebs, therefore, though isomeric with oil of turpen- ontains the hydrocarbon in a more condensed form, viz., as).

Essence of Capivi (*Sp. gr.* 0·878,), which is obtained by ng balsam of capivi with water, appears to belong to the lass as that of cubebs. It boils at 500°, undergoing par- omposition. It yields a crystalline compound with hydro- acid ($C_{30}H_{24}$, 3 HCl).

(1231) 12. *Essence of Hops.*—This essence is obtained
tilling dried hop-cones with water. The oil when first
is of a beautiful green colour, but it is rendered colourless
tification. It remains liquid at 2° F., and begins to boil
284°, but the boiling point rises rapidly till it exceeds 6
odour somewhat resembles that of the hop. When expose
air it becomes converted into an acid resinous mass. Oil
is a mixture of the hydrocarbon $C_{20}H_{16}$, with *valerol* (C
The hydrocarbon may be obtained in a pure form by allo
oil to fall drop by drop upon hydrate of potash, when c
and valerate of potash are formed from the valerol :—

$$\overbrace{C_{12}H_{10}O_2}^{\text{Valerol.}}+3\,(KO,HO)+H_2O_2 = 2\,KO,C_2O_4+\overbrace{KO,C_{10}H_9O_3}^{\text{Valerate of potash.}}+$$

13. *Essence of Valerian* also consists of valerol and of
carbon $C_{20}H_{16}$, which is identical with borneène, the hyd
which accompanies Borneo camphor (1237). By distilling
essence at a temperature of 392°, the borneène may be
Valerol when exposed to a temperature of 32° crysta
transparent prisms, which do not melt until heated to
gradually becomes oxidized by exposure to the air, and
agreeable odour of valeric acid is developed. In its pure
odour is but slight, resembling that of hay. Sulphuric
solves it, and forms a blood-red solution, which contains
gated sulpho-acid.

(1232) 14. *Oil of Thyme.*—This consists of an oxidi
tion, *thymol*, and of a hydrocarbon, *thymene*. The latter
tutes the more volatile portion of the oil; it has an a
odour of the plant: it boils at 329°, and exerts no ac
polarized light. *Thymol*, $C_{20}H_{14}O_2$, is isomeric with car
with cuminic alcohol (1256); it has the agreeable odour of
and constitutes about one half of the essence of thyme.
solid which crystallizes in oblique rhombic prisms: it
111° and boils at 446°, giving off a vapour of sp. gr. of 5
is very soluble in alcohol and in ether. This substance
contained in the oil of horse-mint (*Monarda punctata*),
an Indian plant, the *Ptychotis ajowan*. Thymol combin
sulphuric acid and forms a crystallizable colligated acid,
phothymylic ($HO,C_{20}H_{13}O,S_2O_6$), which is analogous to
phethylic.

According to Lallemand, when thymol is treated with o
agents such as chromic acid, or a mixture of peroxide of
nese and sulphuric acid, it yields a substance termed

O$_4$),* which sublimes in brilliant orange-coloured quadran-
ates, of an aromatic odour and an appearance resembling that
one (1163), with which it is homologous. If treated with
ous acid or other reducing agents, it combines with hydro-
yields *thymoilol* ($C_{24}H_{18}O_4$), the homologue of hydroqui-
nd by mixing a solution of equal weights of thymoil and
ol in boiling alcohol, the liquid immediately becomes of a
d colour, and deposits beautiful violet-coloured prismatic
which have a bronze lustre. These correspond to what
termed green hydroquinone.

Table of Essential Oils not containing Oxygen.

Formula.	Sp. gr. Liquid.	Sp. gr. Vapour.	Boiling point ° F.	Direction of rotation.	Compound with HCl.	Remarks.
$C_{20}H_{16}$	0·864	4·812	318—325°			Many of the oils enumerated in this table contain oxidized compounds in addition to the hydrocarbon, — as may be seen by the formulæ given in this column.
,,	0·843		350	left.	solid.	
,,	0·913		above 680°			
,,	0·86		320	none.	liquid.	
,,	0·843	4·767	273	none.	liquid.	
,,	0·87		273	none.	solid.	
,,	0·869		361	right.		$C_{20}H_{16}$ & $C_{30}H_{10}O_{10}$
,,		4·60	320	left.	solid.	
,,	0·847	5·28	313			Consists of several oils.
,,			347			$C_{20}H_{16}$ & $C_{10}H_8O_2$
,,	0·938	5·17	343	right.	solid.	$C_{20}H_{16}$ & $C_{20}H_{14}O_2$
,,	0·918		289		liquid.	$C_{20}H_{16}$ & $C_{20}H_{12}O_4$
,,	0·849		345	left.	solid & liquid.	
,,				right.		$C_{20}H_{16}$ & $C_{12}H_{10}O_2$
,,	0·86		320	left.	liquid.	
,,	0·851	4·87	343	right.	solid & liquid.	Contain also $C_{20}H_{10}O_{10}$
,,	0·83	4·64	356	right.		
,,			320			Contains an oxide.
,,	0·864	4·73	333		liquid.	
,,			320			
,,	0·837		320			
,,		4·76	329	none.	liquid.	$C_{20}H_{16}$ & $C_{20}H_{14}O_2$
	This hydrocarbon is identical with Borneëne					$C_{20}H_{16}$ & $C_{12}H_{10}O_2$
$C_{20}H_{24}$	0·878		500	left.	solid.	
,,	0·929		490	left.	solid.	$C_{20}H_{24}$ & $C_{20}H_{24}$, 2 HO
$C_{32}H_{26}$	0·984	7·9	458	right.		$C_{32}H_{26}$ & $C_{32}H_{28}O_2$
$C_{20}H_{18}$	0·851	4·94	325			From oil of peppermint.
$C_{40}H_{32}$	0·940		595	none.		
$(CH)_x$			592			

robable that the formula both of quinone and of thymoil should
l as one half of that given by Gerhardt and Lallemand; so that
ould be represented as $C_{12}H_8O_2$, since it is not easy to see how

(1233) *Essences which contain other Hydrocarbon*
of Peppermint.—This essence when distilled with
anhydride, yields a hydrocarbon termed *menthene*, C_{20}
essence also appears to contain a solid hydrate of this
($C_{20}H_{18}$, 2 HO), which is analogous to camphor: this
may be obtained in crystals; it fuses at 93° and boil
emitting a vapour of sp. gr. 5·62.

2. Essence of *Cedar wood* is somewhat analogous in
to the foregoing oil. It consists of a crystallizable solid
—dissolved in a hydrocarbon ($C_{32}H_{26}$), which has be
cedrene.

3. *Attar of Roses* consists also of two compounds, on
has but little odour; it remains solid at temperatures b
and boils at about 590°. It is polymeric with olefiant
fragrant portion is liquid; it contains oxygen, but its c
is not accurately known.

The table on the preceding page includes a list of
important essences which contain unoxidized hydrocarbo

(*B*) *Oxidized Essences.*

(1234) Several varieties of oxidized essential oils ar
viz.:—(*a*) Solid crystallized essences which have the c
of hydrates of a hydrocarbon; these constitute the *ca*
which laurel camphor ($C_{20}H_{14}$, 2 HO) affords the best il
(*b*) *Indifferent* oils, such as spear-mint oil ($C_{20}H_{20}O_2$).
which resemble the *aldehyds*, such as oil of bitter
($C_{14}H_5O_2$,H), and of cinnamon ($C_{18}H_7O_2$,H). (*d*) *Compo*
such as oil of winter-green (salicylate of methyl, C_2H_3O

(1235) (*a*) CAMPHORS.—From the statements alrea
is clear that the camphors are closely related to the
varieties of turpentine. Two species of camphor are kno
east, *Borneo camphor* and *laurel camphor*; the one call
camphor ($C_{20}H_{18}O_2$) is obtained from the *Dryobalanops*
and is so highly prized by the natives of the east that bu
it finds its way into the European market.

Laurel Camphor ($C_{20}H_{16}O_2$): *Sp. gr. of solid* 0·996;
5·3147; *Fusing pt.* 347°; *Boiling pt.* 399°.—This consti
common camphor of the shops. The commercial
furnished by the *Laurus camphora*, but it is also pr

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a body which, like thymol, contains in its molecule only 20
carbon, should by oxidation yield a compound containing 24 eq
carbon.

ll quantity by many other plants, which appear to furnish it he oxidation of their essential oils. This is easily understood, the formula of this substance is the same as that of oil of ntine, to which two equivalents of oxygen have been added. oils of lavender, of rosemary, and of marjoram, and those of ral of the *Labiatæ*, such as the oils of pennyroyal and of spear-, contain camphor in solution. Amber, and the oils of vale- tansy, and sage also yield it when treated with nitric acid.

Three isomeric modifications of camphor are known; they ot be distinguished from each other, except by their action a ray of polarized light: one of the varieties produces rota- of the ray to the right; the second variety produces left- d rotation; whilst the third variety has no sensible effect upon larized ray. The common camphor of the shops, and that ued by the action of nitric acid upon borneène, is the right- d modification. The camphor contained in the oil of *Matri- parthenium* exerts a left-handed rotatory action upon a ray larized light (Chautard); whilst, according to Biot, the cam- deposited by oil of lavender is destitute of any such rotatory upon a polarized ray.

n the ordinary process of extracting camphor, the wood and ches of the camphor laurel are chopped up, and placed with r in a rude kind of still, the head of which is filled with rice . On the application of heat, the camphor rises in vapour with ter, and is condensed in the straw. It is then submitted to a sublimation, by which means it is obtained in the form of de, granular camphor of commerce. This article is subse- refined in this country, by placing charges of 10 lb. or the crude camphor in large globular glass flasks, fur- with a short wide neck: heat is applied to the bottom of flasks by means of a sand bath; and as soon as the camphor ed, a portion of lime is added to each flask, after which the is steadily maintained for forty-eight hours: during this the camphor is slowly sublimed into the upper part of the . When the operation is finished, the flasks are cooled, and at ame time broken, by sprinkling them with cold water: the amphor can then be removed with facility. The produce of peration assumes the form of white, tough, translucent

Camphor has a peculiar odour and an aromatic taste, ot and afterwards cooling. It floats in water, and is soluble in this liquid; but is dissolved freely by alcohol, ic acid, and the essential oils. Although pure camphor nd difficult to pulverize, yet if moistened with a few

may be reduced to powder with facility.
camphor are thrown on water, each
with a remarkable and rapid gyratory
checked by allowing a drop of any
surface of the water. Camphor fuses at
It is very inflammable, and burns with a
It becomes slowly volatilized at common
kept in glass bottles is gradually sublimed, and
crystals on the side of the vessel which
light. If a coil of red-hot platinum wire be
lump of camphor, the metal continues to glow,
combustion of the camphor, which may be
as any portion remains unconsumed.

be heated under pressure with hydrate of
with both the potash and the water; a salt
potash being formed:—

$$\overbrace{C_{20}H_{16}O_2}^{\text{Camphor.}}+KO,HO=\overbrace{KO,C_{20}H_{17}O_3}^{\text{Campholate of potash.}}$$

camphor is distilled with phosphoric
chloride of zinc, it undergoes decomposition,
the elements of water, whilst *cymol* is formed:—

$$\overbrace{C_{20}H_{16}O_2}^{\text{Camphor.}}=H_2O_2+\overbrace{C_{20}H_{14}}^{\text{Cymol.}}$$

Camphoric Acid ($2\,HO,C_{20}H_{14}O_6$).—Camphor,
ten times its weight of concentrated nitric
and becomes converted into *camphoric acid.*
sparingly soluble in water, but is freely
as by ether and the essential oils. It is
ions in the form of prismatic needles, which
they are destitute of odour, and are fusible at
acid is dibasic; it may be deprived of its basic
in the form of anhydride by sublimation.
phoric acid produces a precipitate in a
of lead.

that three isomeric modifications of
pound just described is characterized by its
right-handed rotation of a ray of
Chautard, the camphoric acid obtained by
of the *Matricaria parthenium* with nitric acid.
rotatory action; and if the right-handed
acids be mixed in equivalent

is obtained, which, like racemic acid, is destitute of any
ction upon the plane of polarization: this mixed acid
ewhat in chemical properties from either of its two com-
omptes Rendus*, xxxvii. 166).

Borneo Camphor ($C_{20}H_{18}O_2$); *Fusing pt.* 388°; *Boiling*
-This substance differs from the preceding variety of
n containing 2 atoms more of hydrogen. It is less
l volatile than common camphor, but is denser and
t exerts a right-handed rotatory action upon polarized
its power in this respect is smaller than that of ordinary
from which it can scarcely be distinguished in taste,
bility, and general appearance. It crystallizes in small,
t, regular, colourless, six-sided prisms. If gently warmed
acid of moderate strength, it loses 2 atoms of hydrogen,
verted into ordinary camphor.

camphor occurs in the *Dryobalanops*, in combination
($C_{20}H_{16}$) termed *borneène*, which has the composition of
il of turpentine: the same hydrocarbon also occurs in
al oil of valerian. In order to procure the camphor,
are made into the wood of the growing tree, and the
exudes is submitted to distillation: the borneène is
and an imperfect separation of the camphor and oil is
ed. If borneène be repeatedly distilled with a solution
it combines with 2 atoms of water, and is converted
o camphor. A similar conversion into the same cam-
occurs if the oil be dissolved in an equal bulk of an alco-
ion of potash, and be left at rest in imperfectly closed
r a few days; on dilution with water the camphor is
Borneo camphor, if mixed with phosphoric anhydride
ed, loses two atoms of water, and is reconverted into

on has already been made to other camphors, such as—

bs camphor (1230) . . . . ($C_{30}H_{24}$, 2 HO)
entine camphor (1225) . . . ($C_{20}H_{16}$, 4 HO)
ermint camphor (1233) . . . ($C_{20}H_{18}$, 2 HO),

These compounds, however, are of little importance.

(*b*) *Indifferent essential Oils containing oxygen.*—The
of many of these have been already mentioned when
of the hydrocarbons with which they are associated
33).

of Lavender (*Sp. gr.* 0·898).—The exact composition of
nt and well-known oil has not been accurately ascer-

tained. It is soluble in concentrated acetic acid : when long
it deposits a large proportion of laurel camphor.

2. *Oil of Wormwood* is isomeric with laurel camphor.

Besides these, there are a great variety of essences which
tain oxygen, but which have been but imperfectly examined;
for instance, as the oils of cajeput, of dill, of marjoram, of
royal, of sage, of sassafras, and of many other plants.

(1239) (*c*) *Oils analogous to the Aldehyds.*—The oils of
almonds, of spiræa, of cinnamon, and of cumin are cha
ized by forming crystallized compounds with bisulphite of
and, like the aldehyds of the series homologous with ord
alcohol, they exhibit a strong tendency to form acids
absorption of 2 atoms of oxygen. The oils of thi
however, differ from the ordinary aldehyds in the facility
which they allow the displacement of one atom of th
drogen which they contain by an equivalent of chlorine, of
phur, of cyanogen, and of various electro-negative elements.
have been regarded as hydrides of peculiar oxidized radic
example :—

Oil of bitter almonds .	$C_{14}H_5O_2,H = Bz, H$	Hydride of be
Oil of cumin . . .	$C_{20}H_{11}O_2,H = Cu, H$	Hydride of cum
Oil of cinnamon . .	$C_{18}H_7O_2,H = Ci, H$	Hydride of cin

When these aldehyds are heated with an alcoholic solu
potash they yield the alcohol and the acid of the series (Can
Thus bitter almond oil furnishes the alcohol of the benzo
and benzoic acid :—

$$2\,\overbrace{(C_{14}H_5O_2,H)}^{\text{Ess. bitter almonds.}}+KO,HO=\overbrace{C_{14}H_7O,HO}^{\text{Benzoic alcohol.}}+\overbrace{KO,C_{14}H_5O_3}^{\text{Benzoate of potash.}}$$

In describing these oils it will be convenient to consid
most important derivatives, which are very numerous, and
compounds many of which present several points of intere

In this section the following compounds will be exami

1. Essence of bitter almonds.—Benzoic series.—Hippur
2. Essence of cumin.—Cuminic series.
3. Essence of cinnamon.—Cinnamic series.—Coumarin.
4. Essence of spiræa.—Salicylic series.—Salicin.—Pop
5. Essence of aniseed.—Anisic series.

1. *Essence of Bitter Almonds.—Benzoic Series.*

(1240) The essence of bitter almonds is the most im
member of the group of oxidized essential oils. It form

f a remarkable memoir by Liebig and Wöhler (*Ann. de* II. li. 273), in which they first systematically applied the f compound radicles to substances of organic origin. The on of this paper exercised an immediate and extraordinary upon the study of organic chemistry, in which, indeed, rated a new era, and thus led to a series of brilliant dis- which followed in rapid succession.

following compounds of the benzoic series will be briefly , or the mode of their formation will be indicated :—

in . . .	$C_{40}H_{27}NO_{22}$, 6 Aq	
ic acid .	$HO,C_{40}H_{26}O_{24}$	

---

of benzoyl	$C_{14}H_5O_2,H$	$=BzH$
nzoyl . .	$C_{14}H_5O_2,NO_4$	$=BzNO_4$
of chloro- l . . .	$C_{14}H_5Cl_2,H$	
of benzoyl	$C_{14}H_5O_2,Cl$	$=BzCl$
dride of l . . .	$C_{14}H_5O_2,H+C_{14}H_5O_2,Cl$	$=BzH,BzCl$
of benzoyl	$(C_{14}H_5O_2,S)_2$	$=(BzS)_2$
of do. .	$C_{14}H_5O_2,Br$	$=BzBr$
do. . .	$C_{14}H_5O_2,I$	$=BzI$
f do. .	$C_{14}H_5O_2,C_2N$	$=BzCy$
zoylic acid	$HO,C_{14}H_6O_2,C_2HO_3$	$=HO,BzH,C_2HO_3$
of hydride oyl . .	$2\ C_{14}H_6O_2,C_{14}H_6O_4$	$=2\ BzH,(HO,BzO)$
nate of hy- f benzoyl	$C_{14}H_6O_2,HC_2N$	$=BzH,HCy$
e (hydride o-benzoyl)	$C_{46}H_{18}N_2O_4$	
cid . .	$HO,C_{14}H_5O_3$	$=HO,BzO$
nhydride .	$C_{14}H_5O_3,C_{14}H_5O_3$	$=BzO,BzO$
tic anhy-	$C_{14}H_5O_3,C_4H_3O_3$	$=BzO,\overline{Ac}$
nzoic acid .	$2\ HO,C_{14}H_4S_2O_8$	
zoic acid .	$HO,C_{14}H_4,NO_4,O_3$	
nzoic acid .	$HO,C_{14}H_4,H_2N,O_3$	
le . . .	$H_2N,C_{14}H_5O_2$	$=H_2N,Bz$
de . . .	$C_{12}H_5,HN,C_{14}H_5O_2$	$=C_{12}H_5,HN,Bz$
zamide .	$C_{42}H_{18}N_2$	
limide .	$C_{28}H_{13}NO_2$	
amide .	$C_{44}H_{18}N_2O_2$	

Benzoylic azotide .	$C_{30}H_{12}N_2$
Azobenzoyl . .	$C_{42}H_{15}N_2$
Benzoic alcohol .	$C_{14}H_7O,HO$
Benzo-ether . .	$C_{14}H_7O,C_{14}H_7O$
Toluylia . . .	$C_{14}H_7,H_2N$

Benzoine . . .	$C_{28}H_{12}O_4$	$=C_{28}H_{1}$
Benzile	$C_{28}H_{10}O_4$	
Benzilic acid . .	$HO,C_{28}H_{11}O_5$	$=HO,C$
Chloride of benzile	$C_{28}H_{11}O_4Cl$	$=C_{28}H$
Benzoinamide . .	$C_{84}H_{36}N_4$	
Benzoinam . . .	$C_{56}H_{24}N_2O_2$	

(1241) *Amygdalin* ($C_{40}H_{27}NO_{22}+6\ Aq$).—The pu bitter almond contains a large portion of a bland, near colourless fixed oil, which can be separated from it l and which is identical in properties with that furnis sweet almond; but the kernel does not contain any ready formed. As soon, however, as the pulp is moistened with water, the fragrant odour of the esse ceived. This development of the essential oil is due composition of *amygdalin*, a crystallizable azotised prin is contained in the kernel, in addition to the oi saccharine, and ligneous constituents of the seed.

In order to extract the amygdalin, the cake whi after the fixed oil has been separated by expression is fragments, and digested with hot alcohol of sp. gr. o solution must be filtered, and the alcohol distill syrupy residue must then be diluted with water, mixed and set aside to ferment, in order to decompose the su filtering the liquid and evaporating, the amygdalin cr acicular tufts. It is very soluble in water, from deposited in prisms with 6 Aq. The whole of this wat by a temperature below 250°.

Amygdalin has a sweetish, somewhat bitter taste, poisonous. Its solution exerts a left-handed rotation u polarized light. When it is treated with alkaline so monia is expelled, and a new acid, the *amygdalic* (HO is found in the liquid; this decomposition is analog produced in asparagin under similar circumstances:—

$$\overbrace{2\,C_{40}H_{27}NO_{22}}^{\text{Amygdalin.}}+2\,(KO,HO)+H_2O_2=2\,\overbrace{(KO,C_{40}H_{26}O_{24})}^{\text{Amygdalate of potash.}}+$$

The most remarkable change, however, to which amygdalin is subject, is that which it undergoes when the bruised kernel in which it is contained is brought into contact with water. As soon as this is done, the peculiar and agreeable odour of bitter almonds is perceived; in twenty-four hours all traces of amygdalin will have disappeared, and in its place an essential oil, hydrocyanic acid, sugar, and formic acid will be found. This singular transformation is the result of a species of fermentation produced by the action of a peculiar azotised matter allied to casein, and which resembles the diastase of malt; to this substance the name *synaptase*, or *emulsin*, has been given. This ferment is contained both in the bitter and the sweet almond. If boiling water be poured upon the pulp, the synaptase is coagulated, and no formation of the essence ensues. In preparing the essence, cold water should therefore be employed, and the mixture should be allowed to stand for some hours before proceeding to distillation.*

The change which occurs in amygdalin under the influence of synaptase may be thus represented:—

$$2\,\overbrace{C_{40}H_{27}NO_{22}}^{\text{Amygdalin.}} = 4\,(\overbrace{C_{14}H_5O_2,H}^{\text{Essential oil.}}) + 2\,(\overbrace{H,C_2N}^{\text{Hydrocy. acid.}}) + \overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}} + 4\,(\overbrace{HO,C_2HO_3}^{\text{Formic acid.}})$$
$$+\,3\,H_2O_2.$$

---

* Synaptase is a ferment which may be advantageously applied to many organic compounds in order to effect their transformation into new products. It may be procured from the cake left after the expression of the oil of the sweet almond. This mass must be diffused through a quantity of pure water equal to about thrice its weight; the liquid must be strained through a cloth, and the undissolved portion submitted to pressure. The emulsion thus procured must be left for three or four days at a temperature of 70° or 80°, during which time it becomes separated into two layers; the upper one consisting of a curd-like coagulum, and the lower one forming a clear liquid, like whey. In the course of two or three days this lower stratum ceases to yield any precipitate on the addition of acetic acid: when this point has been reached, alcohol must be added so long as it occasions a precipitate. This precipitate consists of synaptase in combination with phosphates of lime and magnesia: it must be washed with absolute alcohol, and dried *in vacuo* over sulphuric acid.

The synaptase thus obtained cannot be freed from the salts which accompany it, but it is sufficiently pure to enable its action as a ferment to be studied. When dried as directed, it may be preserved unaltered: but if left in a moist condition, it speedily becomes putrid. It is completely soluble in cold water; the liquid has an acid reaction, which enables it to hold the earthy phosphates in solution. In this state it speedily transforms amygdalin into the essence of bitter almonds and other products. The aqueous solution of synaptase becomes turbid when heated, owing to the separation of a portion of the earthy phosphates; the liquid, however, again becomes clear as it cools, but no longer possesses the power of effecting the transformation of amygdalin into hydride of benzoyl. A solution of synaptase is entirely precipitated by one of acetate of lead, and the precipitate so obtained acts upon amygdalin in the same way as *synaptase itself.*

100 parts of amygdalin yield about 41 of the essential oil, and 6 of hydrocyanic acid.

The proportion of hydrocyanic acid liberated by the reaction is perfectly definite, and it has been proposed by Liebig and Wöhler to take advantage of this fact in prescribing hydrocyanic acid medicinally. Amygdalin may be dissolved in water, and it may be kept unchanged; but if it be mixed with an emulsion of sweet almonds, decomposition commences immediately, and the characteristic odour of the essence is developed. Seventeen grains of amygdalin when dissolved in one ounce of emulsion of sweet almonds, would furnish exactly one grain of pure hydrocyanic acid; or it would contain an amount of the acid equivalent to 50 minims of the dilute hydrocyanic acid of the London Pharmacopœia.

Oxidizing agents, such as nitric acid, or a mixture of black oxide of manganese and sulphuric acid, decompose amygdalin with formation of hydride of benzoyl, benzoic acid, formic acid, ammonia, and sometimes carbonic acid from the oxidation of the formic acid:—

$$\overbrace{C_{40}H_{27}NO_{22}}^{\text{Amygdalin.}} + 2\,O_4 = \overbrace{C_{14}H_6O_2}^{\text{Hydride benzoyl.}} + \overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}} + 6\,(\overbrace{HO,C_2HO_3}^{\text{Formic acid.}}) + H_3N.$$

(1242) Essence of Bitter Almonds, or *Hydride of Benzoyl* ($C_{14}H_5O_2,H = 106$); *Sp. gr.* 1·043; *Boiling pt.* 356°.—In order to extract this essence, the bitter almond cake which is left after the expression of the fixed oil is crushed and made into a thin cream with water. It is then introduced into a still, where it is allowed to remain for twenty-four hours, with occasional agitation, in order that the amygdalin may be completely decomposed. At the end of that time the distillation is proceeded with. This operation is best effected by the injection of steam; the liquid is thus speedily raised to the boiling point, and all risk of charring the vegetable matter is averted: the oil passes over as usual with the vapour, and may be condensed in suitable receivers. The distillation must be continued so long as the distillate comes over with a milky appearance.

A considerable quantity of the essence is dissolved in the distilled water, but most of this can be recovered by subjecting the water to a second distillation, the essence coming over with the first portions. The kernels of the peach, the plum, the cherry, and other stone fruit, as well as the leaves of the laurel (*Prunus laurocerasus*), also yield this essence in notable quantities.

The crude essence, in addition to hydride of benzoyl, contains hydrocyanic and benzoic acids, and a crystalline body termed benzoine (1249): it is extremely poisonous, owing to the presence of hydrocyanic acid; but it may be readily purified from the latter compound by agitating the oil briskly with a mixture of milk of lime and protochloride of iron, and then submitting it to distillation.

The purified oil is not poisonous. It is inflammable, and burns with a smoky flame. Hydride of benzoyl is soluble in 30 parts of water, but it is dissolved by alcohol and by ether in all proportions. This oil exerts no rotatory action upon polarized light. It behaves like an aldehyd; for instance, when essential oil of bitter almonds, either in its pure or its rectified condition, is left in contact with the atmosphere and with water, it gradually absorbs oxygen, and is at length wholly converted into a crystalline mass, consisting of benzoic acid:—

$$2\ (\overbrace{C_{14}H_5O_2,H}^{\text{Hydride of benzoyl.}}) + O_4 = 2\ (\overbrace{HO,C_{14}H_5O_2,O.}^{\text{Benzoic acid.}})$$

When oil of bitter almonds is heated with hydrate of potash, it yields hydrogen and the benzoate of the alkali:—

$$\overbrace{C_{14}H_5O_2,H}^{\text{Hydride of benzoyl.}} + KO,HO = \overbrace{KO,C_{14}H_5O_3}^{\text{Benzoate of potash.}} + H_2.$$

Concentrated nitric acid converts the essence into nitro-benzoic acid ($HO,C_{14}H_4,NO_4,O_3$), with brisk evolution of heat; but if the reaction be moderated by the addition of water, a yellowish oil termed *nitro-benzoyl* is formed, which gradually solidifies; it is a compound in which the hydrogen of the hydride has been displaced by peroxide of nitrogen:—

$$\overbrace{C_{14}H_5O_2,H}^{\text{Hydride of benzoyl.}} + HO,NO_5 = \overbrace{C_{14}H_5O_2,NO_4}^{\text{Nitro-benzoyl.}} + H_2O_2.$$

When oil of bitter almonds is treated with perchloride of phosphorus, it yields a compound termed *chlorobenzol* ($C_{14}H_6Cl_2$; *Sp. gr. of liquid* 1·245; *of vapour* 5·625: *Boiling pt.* 403°), in which the oxygen of the essence appears to have been displaced by chlorine, whilst oxychloride of phosphorus is formed, and can be expelled by heat. Chlorobenzol is a limpid, colourless liquid, which has but little odour at ordinary temperatures, but when heated it gives off an irritating vapour. It is insoluble in water, but readily soluble in alcohol and in ether. Limpricht regards this body as the chloride of benzoglycol, the diatomic alcohol of the benzoic series: when treated with salts of silver it yields compounds of benzoglycol; thus:—

$$\overbrace{C_{14}H_6Cl_2}^{\text{Chloro-benzol.}}+2\,(\overbrace{AgO,C_4H_3O_3}^{\text{Acetate of silver.}})+H_2O_2=\overbrace{C_{14}H_8O_4,\ 2\,C_4H_3O_3}^{\text{Binacetate of benzo-glycol.}}+2\ AgCl.$$

On attempting to isolate the benzo-glycol it becomes decomposed into oil of bitter almonds and water, $C_{14}H_8O_4=C_{14}H_6O_2+H_2O_2$.

(1243) *Chloride of Benzoyl,* or *Benzoic Oxychloride* ($C_{14}H_5O_2,Cl = 140{\cdot}5$); *Sp. gr. of liquid* 1·25, Cahours; *of vapour* 4·987; *Boiling pt.* 383°.—When a current of dry chlorine is transmitted through the essential oil of bitter almonds gently warmed, much hydrochloric acid is evolved, and chloride of benzoyl is obtained in the form of a colourless liquid, the vapour of which produces lachrymation; it has a peculiar irritating odour resembling that of horseradish. Chloride of benzoyl burns with a green smoky flame. This substance sinks in water without mixing with it; but if boiled with water, it is gradually dissolved, and decomposed into hydrochloric and benzoic acids; $C_{14}H_5O_2,Cl+H_2O_2=HO,C_{14}H_5O_3+HCl$.

The best method of preparing the chloride of benzoyl, when required in considerable quantity, consists in heating gently in a retort a mixture of 122 parts of crystallized benzoic acid, and 211 of perchloride of phosphorus (1 atom of each substance): a violent reaction occurs, attended with a copious extrication of hydrochloric acid:—

$$\overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}}+PCl_5=\overbrace{C_{14}H_5O_2,Cl}^{\text{Chlor. benzoyl.}}+HCl+\overbrace{PO_2Cl_3}^{\text{Oxychlor. phosph.}};$$

when this has terminated, the mixture is submitted to distillation. As soon as the boiling point rises to 383°, pure chloride of benzoyl passes over, the portions which distil at a lower point consisting of a mixture of oxychloride of phosphorus and chloride of benzoyl. This mixture may be purified by distilling it from anhydrous benzoate of soda, the oxychloride of phosphorus becoming decomposed in the following manner:—

$$3\,(\overbrace{NaO,C_{14}H_5O_3}^{\text{Benzoate of soda.}})+\overbrace{PO_2Cl_3}^{\substack{\text{Oxychlor.}\\\text{phosph.}}}=3\,(\overbrace{C_{14}H_5O_2,Cl}^{\substack{\text{Chloride}\\\text{of benzoyl.}}})+\overbrace{3\,NaO,PO_5}^{\substack{\text{Phosph.}\\\text{of soda.}}}.$$

Chloride of benzoyl has been extensively employed by Gerhardt in the preparation of the anhydrides of the organic acids (1096).

Gaseous ammonia decomposes it, and yields benzamide (1175), and hydrochlorate of ammonia:—

$$\overbrace{C_{14}H_5O_2,Cl}^{\text{Chlor. benzoyl.}}+2\,H_3N=H_4NCl+\overbrace{H_2N,C_{14}H_5O_2}^{\text{Benzamide.}}.$$

Aniline attacks it in a similar manner, and produces *benzanilide* ($C_{12}H_5,HN,C_{14}H_5O_2$).

When mixed with alcohol it yields benzoic ether :—

$$\overbrace{C_{14}H_5O_2,Cl}^{\text{Chlor. benzoyl.}}+\overbrace{C_4H_5O,HO}^{\text{Alcohol.}}=\overbrace{C_4H_5O,C_{14}H_5O_3}^{\text{Benzoic ether.}}+HCl.$$

Sometimes in the reaction of chlorine upon the hydride of benzoyl, brilliant colourless plates of a substance sparingly soluble in cold alcohol are deposited. They are formed by a combination of chloride with hydride of benzoyl ($C_{14}H_5O_2,H+C_{14}H_5O_2,Cl$), which is termed *chlorohydride of benzoyl.*

Sulphide of Benzoyl ($(C_{14}H_5O_2,S)_2$.—When chloride of benzoyl is distilled with sulphide of lead, a yellowish oil of the above composition passes over; it gradually solidifies into a yellow crystalline mass, which has a disagreeable sulphurous odour.

A *bromide of benzoyl* ($C_{14}H_5O_2,Br$), and an *iodide* ($C_{14}H_5O_2,I$) may be obtained by analogous methods, in the form of very fusible crystallizable solids.

Cyanide of benzoyl ($C_{14}H_5O_2,Cy$) may be obtained as a yellow oil, by distilling the chloride of benzoyl with cyanide of mercury.

(1244) *Formobenzoylic* or *Mandelic Acid* ($HO,C_{14}H_6O_2,C_2HO_3$).—When the distilled water of bitter almonds (containing hydrocyanic acid and the essential oil) is boiled with hydrochloric acid, a curious reaction occurs; the hydrocyanic acid is decomposed into ammonia which unites with the hydrochloric acid, and formic acid which enters into combination with the oil of almonds, producing a new body possessed of acid properties, and termed *formobenzoylic* acid :—

$$\overbrace{C_{14}H_6O_2}^{\text{Hydr. of benzoyl.}}+HCl+2\,H_2O_2+\overbrace{H,C_2N}^{\text{Hydrocy. acid.}}=H_4NCl+\overbrace{HO,C_{14}H_6O_2,C_2HO_3}^{\text{Formobenzoylic acid.}}.$$

On evaporating the solution, the acid may be obtained in mixture with hydrochlorate of ammonia, from which it may be separated by ether; the ethereal solution deposits it in rhomboidal tables. It has a sour taste, and is easily soluble in alcohol. When heated, it fuses at a low temperature, emitting an agreeable odour of hawthorn blossoms. Formobenzoylic acid is also obtained by dissolving amygdalin in concentrated hydrochloric acid. Formobenzoylic acid furnishes one of the best instances of the class of colligated acids in which the saturating power of the original acid, the formic, remains unimpaired by its union with the colligate. It forms soluble crystallizable salts with baryta and silver, and with other bases.

A compound *of benzoic acid with hydride* of benzoyl

$[2\ (C_{14}H_5O_2,H)C_{14}H_6O_4]$? is obtained by acting upon the moist essence of bitter almonds with undried chlorine gas; 3 molecules of the essence concur to its formation, but 1 molecule only undergoes oxidation during its production; $6\ C_{14}H_6O_2 + 2\ H_2O_2 + Cl_2 = 2\ HCl + 2\ (2\ C_{14}H_6O_2,C_{14}H_6O_4)$. This reaction presents a certain analogy with that by which acetal (1079) is formed. The benzoic hydride of benzoyl is insoluble in water, but it crystallizes from its alcoholic solution in square prisms, which may be fused at a gentle heat and volatilized without decomposition: it presents none of the characters of an acid. An alcoholic solution of potash gradually decomposes it, and crystals of benzoate of potash are deposited. It appears that under certain circumstances 3 molecules of the essence combine with 1 equivalent of benzoic acid (Laurent and Gerhardt), but the composition of this body is somewhat uncertain.

Hydrocyanate of Hydride of Benzoyl.—If the mixture of hydrochloric acid and the distilled water of bitter almonds be evaporated at a gentle heat, without boiling, a yellow oily liquid of sp. gr. 1·124 is formed; this substance is sparingly soluble in water, but freely so in alcohol and ether. Voelckel states it to be a compound of hydrocyanic acid with hydride of benzoyl ($C_{14}H_6O_2$, HC_2N): it is decomposed into its two components by a temperature of 338°.

The substance to which the name of *benzimide* ($C_{46}H_{18}N_2O_4$)* was given by Laurent, is the result of the action of hydrocyanic acid upon the essence. If the hydride of benzoyl be mixed with a fourth of its bulk of anhydrous hydrocyanic acid, and gently warmed after agitation with an alcoholic solution of potash, white curdy flocculi of *hydride of cyanobenzoyl* (benzimide) are deposited. The same substance is also sometimes met with in the resinous residue of the distillation of the crude essence; and on treating this with boiling alcohol, benzimide is deposited in white flocculi as the liquid cools. Benzimide is sparingly soluble in alcohol and in ether. It fuses on the application of heat, and at a high temperature is decomposed, leaving a carbonaceous residue; fuming sulphuric acid dissolves it with a blue colour, which fades on dilution.

(1245) BENZOIC ACID ($HO,C_{14}H_5O_3 = 9 + 113$); *Sp. gr. of vapour* 4·27; *Fusing pt.* 248°; *Boiling pt.* 462°.—Benzoic acid occurs abundantly in the balsamiferous plants, independently of its artificial origin from bitter almond oil already mentioned.

Gum Benzoin, the produce of the *Styrax Benzoin* of the

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* Laurent stated subsequently that the formula ($C_{28}H_{11}NO_4$) originally given by him for this compound was erroneous.

c archipelago, is the principal source of the supply of ben-
acid. Common benzoin occurs in reddish lumps, which
imes have a lamellated fracture, and contain whitish opaque
s. When recent it emits an odour of bitter almonds. Gum
in appears to be composed of a mixture of three varieties of
with benzoic acid and a small quantity of a fragrant essen-
il. Only one of the resins is soluble in ether, a second is
le in alcohol only. The white opaque masses appear to consist
resin which is soluble in ether: they yield less benzoic acid
the brown portions.

reparation.—Benzoic acid may be extracted from powdered
in by boiling it for some hours with milk of lime, filtering
lution of benzoate of lime from the insoluble compound of
and lime, and, after concentrating the filtrate, adding hydro-
c acid; benzoic acid is thus precipitated, and may be purified by
nation. The acid is, however, generally extracted by the less
mical but simpler process of direct sublimation from gum ben-
which contains 14 or 15 per cent. of the acid: if the resin be
ly powdered and exposed to a temperature of about 300°, the
which exists ready formed in it is expelled, and may be con-
d in suitable receivers. Mohr's plan of conducting the subli-
n, which has been already described when speaking of the
ation of pyrogallic acid (1160), is the simplest and best
d. The resins of tolu and of benzoin when treated with
nitric acid yield an amorphous form of benzoic acid, which
ured yellow with a resinous matter which accompanies it
salts, and hinders them from crystallizing: balsam of tolu
yields nearly half its weight of this acid. This resinous acid
mpletely soluble in boiling water. When this form of the
exposed to the sun's rays, it becomes covered with white
ls of pure benzoic acid; and when sublimed, the ordinary
lline acid is obtained.

roperties.—Benzoic acid assumes the form of white, glisten-
xtremely light, flexible needles, which usually have an agree-
romatic odour, and a hot bitterish taste. The odour, how-
is not due to the acid, but to the presence of a trace of
tial oil which accompanies the acid during the sublimation.
ic acid melts at 248°; it sublimes at 293°, and boils at 462°.
apours are acrid and irritating; when kindled in the open air,
burn with a smoky flame. The acid requires about 200 parts
ater, and 25 of boiling water, for its solution; but it is
solved by alcohol and by ether.

ates.—Most of the benzoates are soluble in water, and in alcohol. If a strong acid, such as the sulphuric or hydrochloric, be added to their aqueous solutions, a crystalline precipitate of benzoic acid is deposited. Potash and ammonia form both normal and acid salts with benzoic acid. *Normal benzoate of potash* ($KO,C_{14}H_5O_3 + Aq = 160 + 9$) crystallizes with difficulty in penniform crystals, which creep up the sides of the vessel during their formation. The *acid benzoate of potash* ($KO,HO,2\,C_{14}H_5O_3$) may be procured from its solution in alcohol, in colourless, pearly tables, which are sparingly soluble in water. It is obtained as a secondary product in the preparation of acetic anhydride by decomposing acetate of potash with chloride of benzoyl. Normal benzoate of *ammonia* is very soluble in water. It is sometimes used as a means of separating iron from nickel and cobalt. If a solution of the normal benzoate of ammonia be allowed to evaporate spontaneously, plates of an acid salt are deposited. The benzoate of *peroxide of iron* falls as a bulky brownish-white gelatinous mass when a neutral solution of a persalt of iron is mixed with one of benzoate of ammonia: perbenzoate of iron is soluble in alcohol. The benzoates of *yttria, zirconia, tin,* and *lead* are insoluble in water; that of *silver* is sparingly soluble in boiling water. A neutral solution of a persalt of iron may be used for detecting the presence of benzoic acid in solution. When any of the benzoates are heated with phosphoric acid, benzoic acid is sublimed, and may be recognised by its characteristic odour. The benzoates of the alkalies and of the earths when submitted to destructive distillation yield a particular hydrocarbon termed *benzol* or *benzine* ($C_{12}H_6$), and a compound termed *benzophenone* or *benzone* ($C_{12}H_5,C_{14}H_5O_2$); these substances are intimately related to the *phenic* group of compounds, which will be described in the chapter upon the products of destructive distillation. *Benzone* stands in the same relation to benzoic acid that acetone does to acetic acid; for example:—

$$2\,(\overbrace{CaO,C_4\,H_3O_3}^{\text{Acetate lime.}}) = 2\,CaO,C_2O_4 + \overbrace{C_6\,H_6\,O_2}^{\text{Acetone.}};$$

$$2\,(\overbrace{CaO,C_{14}H_5O_3}^{\text{Benzoate lime.}}) = 2\,CaO,C_2O_4 + \overbrace{C_{26}H_{10}O_2}^{\text{Benzone.}}.$$

When benzoate of lime and formiate of lime are distilled in the proportion of one equivalent of each, hydride of benzoyl is the result (Piria):—*

$$\overbrace{CaO,C_{14}H_5O_3}^{\text{Benzoate of lime.}} + \overbrace{CaO,C_2HO_3}^{\text{Formiate of lime.}} = 2\,CaO,C_2O_4 + \overbrace{C_{14}H_6O_2}^{\text{Hydride of benzoyl.}}.$$

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[*] Piria finds that cinnamic, cuminic, and other aldehyds may be obtained *by distilling* the salts of their corresponding acids with formiate of lime. Thus *a mixture* of cinnamate and formiate of lime yields oil of cinnamon.

nzoic acid is dissolved by oil of vitriol, and is precipitated ged on dilution with water; but fuming sulphuric acid ts it into a dibasic compound acid, the *benzosulphuric* (2 HO, S_2O_5). Fuming nitric acid converts the benzoic into *nitro-c acid* ($HO,C_{14}H_4NO_4,O_3$); and a mixture of oil of vitriol tric acid produces *dinitrobenzoic acid* ($HO,C_{14}H_3,2\,NO_4,O_3$). ine produces not less than three chlorinated acids: viz., *nated*, *dichlorinated*, and *trichlorinated* benzoic acid, in which nd 3 atoms of hydrogen respectively are displaced by a ponding number of atoms of chlorine. When benzoic acid ted with perchloride of phosphorus it yields chloride of yl in abundance (1243).

enzoic anhydride ($C_{14}H_5O_3,C_{14}H_5O_3$).—This compound is ed by decomposing anhydrous benzoate of soda with chloride zoyl, or with oxychloride of phosphorus (1096). The result reaction is washed with water weakly alkalized with car- of soda: benzoic anhydride is left in the form of a white, mass insoluble in water, but soluble in ether and in hot rous alcohol, from which it crystallizes in oblique prisms. lts at about 108° F., and after undergoing fusion it long s liquid, emitting a peculiar odour, recalling that of benzoic with a slight smell of oil of bitter almonds. It may be d unaltered at 590°. Boiling water slowly converts it into drated acid; the change is hastened by the addition of an

It enters into the formation of many double anhydrides such, for example, as *benzoacetic anhydride* ($C_{14}H_5O_3$, $_3$), which is obtained by heating acetic oxychloride ($C_4H_3O_2Cl$) ried benzoate of soda. A brisk reaction occurs at ordinary atures; when this is over, the residue must be washed water, and with a weak solution of carbonate of soda: etic anhydride is left in the form of a neutral oil, which is than water, and emits an agreeable odour of sherry wine. water slowly decomposes it into a mixture of acetic and acids; but the solutions of the alkalies or of their car- quickly convert it into acetate and benzoate of the base. be distilled without experiencing decomposition: acetic passes over first, and if the distillation be stopped as soon temperature of the boiling liquid reaches 536°, the residue tort solidifies on cooling into a mass of crystallized benzoic

Benzamic acid; Carbanilic acid or *Amido-benzoic acid* $=HO,C_{14}H_4,H_2N,O_3$), as it is more appropriately not a true amidated acid (1166), but benzoic acid in which an atom of hydrogen has been displaced by an lent of amidogen. It is isomeric with anthranilic acid and with salicylamide, and is obtained by the action of agents upon nitrobenzoic acid. If an alcoholic solution benzoic acid be saturated with ammonia and with sulp hydrogen, and then boiled, it becomes green, and a deposit of sulphur occurs: this operation must be repeate three times, in order to complete the decomposition of t benzoic acid :—

$$HO,C_{14}\overbrace{H_4.NO_4.O_3}^{\text{Nitrobenzoic acid.}}+3\,H_2S_2=\overbrace{HO,C_{14}H_4(H_2N)O_3}^{\text{Amidobenzoic acid.}}+2\,H_2O_2+$$

The liquid must be evaporated to the consistence of syru saturated with acetic acid, and the precipitate drained up tiles. It must then be redissolved in boiling water; the digested with animal charcoal, filtered, and allowed to cr Amido-benzoic acid crystallizes in radiated tufts of delicate which are readily soluble in alcohol and in ether. It has sourish taste, but no odour. It forms an insoluble green tate when mixed with salts of copper; with salts of silver a white curdy precipitate, which if left in the liquid crystalline.

This acid likewise possesses the property of combining w acids. Oil of vitriol dissolves amido-benzoic acid by the ai and on cooling, it deposits brilliant crystals ($2\,C_{14}H_7NO_4$, 2 + 2 Aq), which may be recrystallized from boiling water alcohol: their aqueous solution has an extremely sweet t similar compound ($C_{14}H_7NO_4.HO,NO_5$) may be formed w acid. Phosphoric, oxalic, hydrochloric, and other ac with amido-benzoic acid similar combinations. The c with hydrochloric acid forms a crystalline double salt with b of platinum.

Amido-benzoic acid is the representative of a class pounds which the aromatic acids furnish when their nitr tives are submitted to reduction. In this manner am ($HO,C_{16}H_6,H_2N,O_3$), *amido-cuminic* ($HO,C_{20}H_{10},H_2N$,(*amido-anisic* acids ($HO,C_{16}H_6,H_2N,O_5$) may be procured. exhibit a similar tendency to combine with acids, as wel bases; and if the silver salt of one of these acids, such amido-benzoate of silver, be treated with chloride of b compound crystallizable acid is obtained, analogous to the and cuminuric (1252) which are procured by similar trea the compound of glycocine and oxide of zinc:—

$$\overbrace{AgO,C_{14}H_6NO_3}^{\text{Amido-benz. silver.}}+\overbrace{C_{14}H_5O_2Cl}^{\text{Chlor. benzoyl.}} = AgCl+\overbrace{HO,C_{28}H_{10}NO_5}^{\text{New acid.}}.$$

e so-called amido-acids appear to be isologous with glycocine 4) and its homologues, and resemble them considerably in erties.*

By the action of reducing agents upon dinitro-benzoic acid, a ound ($C_{14}H_8N_2O_4$) analogous to the amido-benzoic acid, having omposition of *diamidobenzoic acid*, [$HO,C_{14}H_3(H_2N)_2O_3$] has obtained (Voit), but it possesses none of the characters of an ; it combines readily with acids, the introduction of the second alent of amidogen having given it a decided basic energy.

1247) *Action of Ammonia on the Oil of Bitter Almonds.*—al compounds are produced by the action of ammonia upon ssence, which are different according as the essence employed e, or contains hydrocyanic acid. If it be pure, hydrobenza- and dibenzoylimide are the result of the reaction: if it be in ude state, the hydrocyanic acid takes part in the reaction, enzhydramide and benzoylic azotide are formed.

Hydrobenzamide ($C_{42}H_{18}N_2$) is the most interesting of these

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Griess (*Proceed. Roy. Soc.*, ix. 594, x. 309 and 591) has described a f azotised bodies in some measure connected with the amidic bases. new bodies are generated by the action of nitrous acid upon alcoholic ns of amido-acids of the benzoic group, the change consisting in the sub- n of one atom of nitrogen for three atoms of hydrogen in two molecules mido-acid. When, for example, amido-benzoic acid is dissolved in alcohol, ge yellow crystalline precipitate is obtained, constituting a dibasic acid e in water, in alcohol, and in ether, but soluble in the alkalies, forming m crystallizable salts which yield precipitates with acetate of lead and trate of silver. The reaction by which it is formed may thus be repre- —

$$\overbrace{4\,C_{14}H_7NO_4}^{\text{Amido.benzoic acid.}}+(NO_3)_2 = 3\,H_2O_2+\overbrace{2\,C_{28}H_{11}N_3O_8}^{\text{New acid.}}.$$

ilar substitution of 1 atom of nitrogen for 3 atoms of hydrogen was by Griess upon aniline and nitraniline, 2 molecules of each compound ked into 1 molecule of the new body; for example:—

$$\overbrace{4\,C_{12}H_7N}^{\text{Aniline.}}+(NO_3)_2 = 3\,H_2O_2+\overbrace{2\,C_{24}H_{11}N_3}^{\text{New compound.}}.$$

queous solution of the amido-benzoic acid be decomposed by nitrous ogen is liberated abundantly, and a new compound, the *oxybenzoic* O,$C_{14}H_5O_5$) of Gerland is obtained. It is metameric with salicylic does not crystallize easily. It furnishes very soluble salts with the and sparingly soluble crystalline compounds with the alkaline earths. ic acid is sparingly soluble in cold water and alcohol. It fuses when d may be sublimed without alteration. The reaction by which it is may be thus represented:—

$$\overbrace{2\,C_{14}H_7NO_4}^{\text{Amido-benzoic acid.}}+(NO_3)_2 = \overbrace{2\,C_{14}H_6O_6}^{\text{Oxybenzoic acid.}}+H_2O_2+2\,N_2.$$

N N

compounds; it may be formed by simply agitating the oil with a solution of ammonia, and afterwards leaving it at rest for some days at the ordinary temperature: but the reaction is completed in a few hours if the mixture be heated to the boiling point. In either case the mixed liquids gradually become converted into a crystalline mass of hydrobenzamide, which must be washed with ether and crystallized from boiling alcohol:—

$$3\,\overbrace{C_{14}H_6O_2}^{\text{Hydr. benzoyl.}} + 2\,H_3N = \overbrace{C_{42}H_{18}N_2}^{\text{Hydrobenzamide.}} + 3\,H_2O_2.$$

Hydrobenzamide forms colourless octohedra with a rhombic base. It is destitute of odour, and insoluble in water, but readily soluble in ether. It melts at 230°; and, if heated for some time to about 260°, or if boiled with a solution of potash, it is converted into the isomeric base termed amarine or benzoline (1198).

When hydrobenzamide is fused with potash, several new compounds are formed, such as *benzostilbine* ($C_{31}H_{11}O_2$?), and *benzolone* ($C_{11}H_4O$?), whilst the nitrogen is expelled in the form of ammonia.

Hydrobenzamide, when boiled with hydrochloric acid, is decomposed; sal ammoniac is formed, and hydride of benzoyl is set at liberty. A similar change is also produced by mere boiling of its alcoholic solution, but the ammonia in that case is liberated in the uncombined form.

2. *Dibenzoylimide* ($C_{28}H_{13}NO_2$) is obtained by passing ammoniacal gas into an alcoholic solution of essential oil of bitter almonds. It is gradually separated in the form of a resinous mass which is soluble in boiling alcohol, and from which it is deposited as a yellowish powder composed of brilliant feathery crystals (Robson):—

$$2\,\overbrace{C_{14}H_6O_2}^{\text{Hydr. benzoyl.}} + H_3N = \overbrace{C_{28}H_{13}NO_2}^{\text{Dibenzoylimide.}} + H_2O_2.$$

3. *Benzhydramide,* or *Hydride of Cyanazobenzoyl a,*—($C_{44}H_{18}N_2O_2$) was originally stated by Laurent to be isomeric with hydrobenzamide, but when he re-examined this substance conjointly with Gerhardt, this statement was ascertained to be an error. If the crude essence of bitter almonds be heated to 212°, and saturated with ammonia, then dissolved in a mixture of alcohol and ether and left to itself for three or four days, a deposit is formed which consists of two portions, viz., *benzhydramide*, and *benzoylic azotide:* they may be separated by the action of boiling alcohol. Benzhydramide is soluble in boiling alcohol, from which on cooling and spontaneous evaporation it is deposited in small brilliant

, which are freely soluble in ether; and which, when boiled ydrochloric acid, are decomposed into hydrocyanic acid, hlorate of ammonia, and hydride of benzoyl.

The portion which is left undissolved by alcohol is the ic *azotide* of Laurent. It is in the form of a white crys- powder, which is nearly insoluble in alcohol and in ether: on the application of heat, and crystallizes on cooling.

The formation of these two compounds is explained by the ing equations :—

$$3\,\overbrace{C_{14}H_6O_2}^{\text{Hydride of benzoyl.}} + \overbrace{H,C_2N}^{\text{Hydrocy. acid.}} + H_3N = \overbrace{C_{44}H_{18}N_2O_2}^{\text{Benzhydramide.}} + 2\,H_2O_2;$$

$$2\,C_{14}H_6O_2 + H,C_2N + H_3N = \overbrace{C_{30}H_{12}N_2}^{\text{Benzoylic azotide.}} + 2\,H_2O_2.$$

5. *Azobenzoyl* ($C_{42}H_{15}N_2$) is a third substance which was ob- d by Laurent. It is nearly insoluble in alcohol, but soluble her: on the application of heat it fuses into a transparent , resembling gum in appearance.

248) *Alcohol of the Benzoic Series* ($C_{14}H_7O, HO$; Cannizzaro): r. *of liquid* 1·059; *of vapour* 3·84; *Boiling pt.* 400°.—In to obtain this compound the following process is adopted :— f bitter almonds is dissolved in its own volume of alcohol, this liquid is mixed with three or four times its bulk of an olic solution of hydrate of potash (of sp. gr. 1·020): a con- ble evolution of heat occurs, and a copious deposition of als of benzoate of potash takes place: when this reaction has nated, boiling water is added to the liquid in quantity suffi- to dissolve the benzoate. The greater part of the alcohol then be distilled off, and more water added to dissolve the ate if necessary; the turbid liquid thus obtained must be d with ether, and the ethereal layer which separates on ing, must be drawn off and subjected to distillation. The portions consist of ether, but subsequently pure benzoic ol passes over. The reaction of the potash upon the hydride zoyl may be thus represented :—

$$\overbrace{2\,C_{14}H_6O_2}^{\text{Hydride of benzoyl.}} + KO,HO = \overbrace{KO,C_{14}H_5O_3}^{\text{Benzoate of potash.}} + \overbrace{HO,C_{14}H_7O.}^{\text{Benzoic alcohol.}}$$

nzoic alcohol is a colourless oily liquid, which is readily d by nitric acid at a gentle heat into oil of bitter almonds; ransformed by chromic acid into benzoic acid: both of ducts are the results of oxidation, which may be thus d :—

$$2\,\overbrace{C_{14}H_8O_2}^{\text{Benzoic alcohol.}}+O_4 = \overbrace{2\,C_{14}H_6O_2}^{\text{Oil of bitter almonds.}}+2\,H_2O_2;\ \text{and}$$

$$C_{14}H_8O_2+O_4 = \overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}}+\ H_2O_2.$$

It is obvious that oil of bitter almonds and benzoic ac in the same relation to benzoic alcohol, that aldehyd an acid do to ordinary alcohol (*vide* Table, p. 149).

If benzoic alcohol be distilled from hydrate of pota decomposed into benzoate of potash and the hydrocarbon k toluol, which corresponds to olefiant gas in the alcohol seri

$$3\,\overbrace{C_{14}H_8O_2}^{\text{Benzoic alcohol.}}+KO,HO=\overbrace{KO,C_{14}H_5O_3}^{\text{Benz. potash.}}+2\,\overbrace{C_{14}H_8}^{\text{Toluol.}}+2\,H_2O_2$$

Benzoic alcohol may be made to yield a series of ethers, which are the following :—

Benzo-ether	$C_{14}H_7O,C_{14}H_7O$	about
Benzo-hydrochloric ether . .	$C_{14}H_7Cl$	about
Benzo-acetic ether	$C_{14}H_7O,C_4H_3O_3$	
Benzo-benzoic ether . . .	$C_{14}H_7O,C_{14}H_5O_3$	

Benzo-ether is obtained by heating benzoic alcohol with anhydride in a closed vessel to about 250° for several The boracic acid must then be extracted with boiling water weak solution of carbonate of soda, and the residue must tilled at a temperature of about 590°; benzo-ether passe and a hydrocarbon ($C_{28}H_{12}$) remains in the retort :—

$$4\,\overbrace{C_{14}H_8O_2}^{\text{Benzoic alcohol.}}=\overbrace{(C_{14}H_7O)_2}^{\text{Benzo-ether.}}+C_{28}H_{12}+3\,H_2O_2.$$

Benzo-hydrochloric ether when heated in a sealed tu ammonia furnishes the volatile base *toluylia*, $C_{14}H_9N$, whi responds to ethylia in the ethylic series. When benzoic al mixed with oil of vitriol, it yields a compound acid (HO,C S_2O_6), corresponding to the sulphethylic. It may be obta crystalline plates.

(1249) BENZOINE ($C_{28}H_{12}O_4$).—It has been already me that when the vapour of hydride of benzoyl is transmitt heated hydrate of potash, benzoate of potash and hydro produced : but if the crude essence be agitated with its ow of a saturated alcoholic solution of potash, the oil is slowly c into a mass of crystals, which are isomeric with the hyd benzoyl : the same change occurs if the pure hydride be d with an alcoholic solution of cyanide of potassium : to th stance thus formed the name of *benzoine* has been given. The presence of hydrocyanic acid is necessary to the production of this metamorphosis; but the mode in which it acts is entirely unknown, since it remains in the liquid, unaltered in amount, after the change has been effected.

Benzoine may be obtained in a state of purity by crystallizing it from boiling alcohol, in which it is readily soluble. Ether also dissolves it freely. It is nearly insoluble in cold water, but is somewhat soluble in boiling water. Benzoine is destitute of odour and of taste: at 248° it fuses, and at a higher temperature it may be distilled unaltered. If its vapour be transmitted through red-hot tubes, it is re-converted into the essential oil of bitter almonds. Cold sulphuric acid dissolves it with the production of a violet colour. Benzoine has been regarded as $(C_{28}H_{11}O_4,H)$, or as the hydride of a new radicle *stilbyl* $(C_{28}H_{11}O_4)$, but the series to which it gives rise has been hitherto but incompletely investigated. When benzoine is fused with hydrate of potash, it becomes converted into benzoate of that base with evolution of hydrogen: but if it be boiled with an alcoholic solution of potash, a beautiful violet-coloured solution is formed which is gradually bleached by boiling, whilst hydrogen is disengaged, and *benzilic acid* remains in combination with the potash:—

$$\overbrace{C_{28}H_{12}O_4}^{\text{Benzoine.}}+KO,HO=\overbrace{KO,C_{28}H_{11}O_5}^{\text{Benzilate of potash.}}+H_2.$$

Benzilic or *Stilbylic Acid* $(HO,C_{28}H_{11}O_5)$ is obtained by decomposing a hot solution of the benzilate of potash, by means of hydrochloric acid: it crystallizes from the solution on cooling, in brilliant needles. Benzilic acid is sparingly soluble in cold water, but is freely dissolved by alcohol and by ether; at 248° it melts to a colourless liquid, which becomes red at a higher temperature; when heated still more strongly it is decomposed, emitting fumes of benzoic acid, and violet vapours; the latter may be condensed into a reddish, acrid, oily liquid. Benzilic acid is soluble in oil of vitriol with a beautiful crimson colour, which disappears on diluting the solution. The benzilates are monobasic; those of silver and lead are white and nearly insoluble.

(1250) *Benzile* $(C_{28}H_{10}O_4)$.—When a current of chlorine is transmitted through melted benzoine, so long as hydrochloric acid is evolved, hydrogen is removed and benzile is formed. It may also be obtained more readily by heating benzoine gently with twice its weight of concentrated nitric acid; benzile rises to the surface in the form of a liquid oil which solidifies on co it may be purified by crystallization from ether or from a and is deposited in beautiful regular six-sided prisms, which a yellowish colour. Benzile is tasteless, and insoluble in It may be fused, and it solidifies again between 194° an into a fibrous mass. At a higher temperature it may be d unaltered. Benzile is polymeric with benzoyl.* It c two equivalents less of water than normal benzilic acid. dissolved in a hot solution of potash it forms a violet-c liquid, which by boiling becomes colourless; the benzile assim one equivalent of water and becoming converted into benz potash; $C_{28}H_{10}O_4+KO,HO = KO,C_{28}H_{11}O_5$.

Benzile is soluble in about 6 parts of acetic acid, this solution be digested with iron it is reconverted into be the hydrogen liberated by the iron at the moment of its s recombining with the benzile (Zinin).

Zinin states that if benzile be treated with an equ amount of pentachloride of phosphorus, *chlorobenzile*, a crystalline compound, is obtained, in which 2 atoms of c have displaced 2 of oxygen, according to the equation :—

$$\overbrace{C_{28}H_{10}O_4}^{\text{Benzile.}}+PCl_5=\overbrace{C_{28}H_{10}Cl_2O_2}^{\text{Chlorobenzile.}}+PCl_3O_2.$$

If alcoholic solutions of chlorobenzile and hydrate of be heated together, equivalent quantities of hydride of benz benzoate of potash are formed, the resulting changes be following :—

$$\overbrace{C_{28}H_{10}Cl_2O_2}^{\text{Chlorobenzile.}}+3\,(KO,HO)=\overbrace{KO,C_{14}H_5O_3}^{\text{Benz. potash.}}+\overbrace{C_{14}H_6O_2}^{\text{Hydr. benzoyl.}}+2\,KCl+H$$

When benzile is treated with ammonia it gives rise to a of compounds which contain nitrogen, viz. :—

$$1.\quad \overbrace{C_{28}H_{11}N\,O_2}^{\text{Imabenzile.}}= \overbrace{C_{28}H_{10}O_4}^{\text{Benzile.}}+H_3N-H_2O_2;$$

$$2.\quad \overbrace{C_{56}H_{22}N_2O_4}^{\text{Benzilimide.}}=2\,C_{28}H_{10}O_4+2\,H_3N-2\,H_2O_2;$$

$$3.\quad \overbrace{C_{56}H_{18}N_2}^{\text{Benzilam.}}\ =2\,C_{28}H_{10}O_4+2\,H_3N-4\,H_2O_2.$$

Chloride of Stilbyl, or *of Benzile* ($C_{28}H_{11}O_4$, Cl) : *Boi* about 518°.—When perchloride of phosphorus is heated with benzilic acid, a violent reaction occurs, chloride of benzile, oxychloride of phosphorus, and hydrochloric acid being formed :—

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* If benzoate of copper be cautiously distilled, an oily distillat over with the odour of geranium. It crystallizes in oblique rhomboidal which fuse at 158°. It may be regarded as *benzoyl* $(C_{14}H_5O_2)_2$, the r the benzoic series. When heated with hydrate of potash it is rea verted into benzoate of potash while hydrogen escapes; (C $2\,(KO,HO)=2\,(KO,C_{14}H_5O_3)+H_2$.

$$\overbrace{HO,C_{28}H_{11}O_5}^{\text{Benzilic acid.}}+PCl_5=\overbrace{C_{28}H_{11}O_4,Cl}^{\text{Chloride of stilbyl.}}+HCl+\overbrace{PO_2Cl_3}^{\text{Oxychlor. phosph.}}.$$

By collecting those portions which distil at a temperature above 482°, chloride of benzile is obtained in the form of a colourless oil which is denser than water. It has a powerful and peculiar odour; on exposure to air it absorbs moisture, and is converted into benzilic and hydrochloric acids; $C_{28}H_{11}O_4, Cl+H_2O_2=HO, C_{28}H_{11}O_5+HCl$.

(1251) Benzoine combines with ammonia, and forms two crystallizable products, which are obtained by digesting benzoine for several weeks in an aqueous solution of ammonia, viz. :—

$$1.\quad \overbrace{C_{84}H_{36}N_4}^{\text{Benzoinamide.}}=3\,\overbrace{C_{28}H_{12}O_4}^{\text{Benzoine.}}+4\,H_3N-6\,H_2O_2;$$

$$2.\quad \overbrace{C_{56}H_{24}N_2O_2}^{\text{Benzoinam.}}=2\,C_{28}H_{12}O_4+2\,H_3N-3\,H_2O_2.$$

Benzoinamide is polymeric with hydrobenzamide; when heated, it melts, and may be distilled unchanged. It is very sparingly soluble both in alcohol and in ether, even at a boiling temperature.

Besides the compounds already described, there are numerous others derived from the essence of bitter almonds which contain sulphur; but for a description of them the reader is referred to Gerhardt's *Traité de Chimie Organique*, tom. iii., and to various memoirs there cited; particularly to one by Laurent (*Ann. de Chimie*, III. i. 291).

(1252) Hippuric Acid ($HO, C_{18}H_8NO_5=9+170$).—This acid is a constituent of the urine of the herbivora, and is most readily obtained from the urine of the cow, which, according to Boussingault, contains about 1·3 per cent. of it. The urine of the horse also yields hippuric acid if the animal be kept at rest, but if he be kept actively at work the greater part of the hippuric acid disappears, and benzoic acid is found in its stead. Hippuric acid, in minute quantity, is also a normal constituent of human urine, but its amount may be voluntarily increased by taking benzoic acid in any form into the system, since benzoic acid during its passage through the human body becomes converted into the hippuric, and is excreted in this form by the kidneys. If the urine be allowed to become putrid, the hippuric acid is decomposed, and benzoic acid is formed in its place. The facility with which these changes occur is explained by the fact that hippuric acid is truly a colligated benzoic compound. When hippuric acid is boiled for some hours with concentrated hydrochloric acid, it assimilates the elements of water and is resolved into benzoic acid and glycocine, in the following manner:—

$$\overbrace{HO,C_{18}H_8NO_5}^{\text{Hippuric acid.}}+H_2O_2=\overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}}+\overbrace{HO,C_4H_4NO_3}^{\text{Glycocine.}}.$$

Dessaignes has also shown that hippuric acid may be reproduced from chloride of benzoyl and the compound of oxide of zinc with glycocine:—

$$\overbrace{C_{14}H_5O_2Cl}^{\text{Chloride of benzoyl.}}+\overbrace{ZnO,C_4H_4NO_3}^{\text{Oxide of zinc and glycocine.}}=ZnCl+\overbrace{HO,C_{18}H_8NO_5}^{\text{Hippuric acid.}}.$$

Preparation.—Hippuric acid may be obtained by adding milk of lime to the fresh urine of cows, boiling for a few minutes, straining from the precipitated phosphates, then adding hydrochloric acid to exact neutralization, and boiling the liquid down to one-eighth of its original bulk; on adding hydrochloric acid in considerable excess to this concentrated liquid, brown crystals of hippuric acid are deposited; they may be dissolved in hot water, and decolorized by transmitting a current of chlorine: the solution on cooling deposits long, colourless, transparent needles of hippuric acid. These crystals often become milk-white when kept.

Properties.—Hippuric acid crystallizes in forms derived from the rhombic prism. It requires about 600 times its weight of cold water for solution, and is still less soluble if this liquid be strongly acidulated with hydrochloric acid; boiling water dissolves it readily, so does hot alcohol, but it is nearly insoluble in ether. Hippuric acid has a bitterish taste; its solutions redden litmus powerfully. The acid melts at a gentle heat, and appears to enter into ebullition at about 464°, but it is in reality becoming decomposed; the distillate contains a crystalline sublimate of benzoic acid, and a reddish oil (benzonitrile) which has the agreeable odour of the Tonka bean: hydrocyanic acid is also formed at the same time, and a considerable residue of carbon is left in the retort.

Hippurates.—Hippuric acid is monobasic. Its compounds with the alkalies and with magnesia are very soluble, and are crystallized with difficulty. Acid hippurates of potash and of ammonia may be obtained. *Hippurate of lime* ($CaO,C_{18}H_8NO_5+3\,Aq$) crystallizes in beautiful rhombic prisms. The *hippurate of lead* is deposited from concentrated solutions in the form of a dense curdy precipitate, but it may be obtained from very dilute *boiling* solutions in tufts of silky needles with 2 Aq, which gra-become changed into broad brilliant quadrangular plates $,C_{18}H_8NO_5+3$ Aq).

olutions of the hippurates give white insoluble precipitates the salts of silver and of mercury: with the persalts of iron yield a characteristic brown precipitate. The hippurates in the solid form are readily distinguished by distilling them hydrate of potash, when they furnish ammonia and benzol.

Hippuric acid is soluble in concentrated nitric acid, and if this tion be mixed with a equal bulk of sulphuric acid, carefully ding any elevation of temperature, it produces a *nitro-hippuric* $(HO,C_{18}H_7,NO_4,NO_5)$, which, when the solution is diluted with e times its bulk of water, is gradually deposited in crystals. he solution of this acid be boiled with sulphuric or hydrochloric it is converted into nitrobenzoic acid and glycocine.

By boiling hippuric acid with a strong solution of potash, it esolved into a benzoate of the base, and into glycocine. It is resolved into benzoic acid and glycocine when boiled with entrated hydrochloric acid; and a similar change occurs if te sulphuric, nitric, or oxalic acid be employed instead of the rochloric.

Considerable difference of opinion has prevailed respecting the ure of hippuric acid, but the reaction of chloride of benzoyl the compound of oxide of zinc with glycocine seems to favour view that this acid is *benzoyl-glycocine*, or glycocine in which atom of hydrogen has been displaced by its equivalent of oyl, the nearly neutral character of glycocine being changed at of an acid by the addition of the electro-negative radicle oyl :—

$$\overbrace{HO,C_4H_4NO_3}^{\text{Glycocine.}} \quad ; \quad \overbrace{HO,C_4H_3(C_{14}H_5O_2)NO_3}^{\text{Hippuric acid, or benzoyl-glycocine.}}.$$

This view is strengthened by the fact that when hippuric acid iled with peroxide of lead, carbonic acid is evolved, and benide is formed; the oxygen in the peroxide of lead producing hange in the manner illustrated by the following equation :—

$$\overbrace{HO,C_4H_3(C_{14}H_5O_2)NO_3}^{\text{Hippuric acid.}})+3\,O_4=2\,H_2O_2+4\,C_2O_4+2\,\overbrace{(H_2N,C_{14}H_5O_2)}^{\text{Benzamide.}}.$$

essaignes has also recently succeeded in procuring hippuric thetically by exposing a mixture of equivalent quantities zine and benzoic acid in a sealed glass tube for some hours perature of 320° or upwards.

urs finds that by treating the compound of glycocine e of zinc with chloride of cumyl and with chloride of anisyl, he obtains crystalline acids corresponding to hippuric in composition—*cuminuric* acid, consisting of ($HO,C_{24}H_{14}NO_5$) and *anisuric* acid of ($HO,C_{20}H_{10}NO_7$).

(1253) *Benzoglycolic Acid* ($HO,C_{18}H_7O_7$).—Strecker was disposed to regard hippuric acid as an amidated acid; and in order to test this theory he subjected it to the action of nitrous acid, which would liberate the dibasic acid of which it was supposed to be the amidic compound if this view were true. Instead of this he obtained a new monobasic acid, which he termed the *benzoglycolic*, since it is evidently a compound of the benzoic and glycolic acids. Benzoglycolic acid may be obtained by exposing a solution of hippuric acid in nitric acid to the action of a current of binoxide of nitrogen, in which case nitrogen gas is evolved, and benzoglycolic acid is formed. This compound is produced by the reaction of nitrous acid upon hippuric acid, and the action of the binoxide of nitrogen on the nitric acid merely presents nitrous acid in the nascent condition to the hippuric acid; $2\ NO_2+NO_5=3\ NO_3$. The reaction of nitrous acid upon hippuric acid may be thus represented:—

$$\overbrace{2\,(HO,C_{18}H_8NO_5)}^{\text{Hippuric acid.}}+(NO_3)_2=\overbrace{2\,(HO,C_{18}H_7O_7)}^{\text{Benzoglycolic acid.}}+H_2O_2+2\,N_2.$$

Benzoglycolic acid crystallizes in rhomboidal prisms, or in thin plates. It is sparingly soluble in cold water, but is freely dissolved by alcohol and by ether. Boiling water also dissolves, but gradually decomposes it; if the acid be heated with a quantity of water insufficient for its solution, it melts to an oily-looking liquid; when heated with dilute acids, it is resolved into benzoic and glycolic acids:—

$$\overbrace{2\,(HO,C_{18}H_7O_7)}^{\text{Benzoglycolic acid.}}+2H_2O_2=\overbrace{2\,(HO,C_{14}H_5O_3)}^{\text{Benzoic acid.}}+\overbrace{2\ HO,C_8H_6O_{10}}^{\text{Glycolic acid.}}.$$

Strecker and Socoloff also obtained a compound of benzoic with lactic acid termed *benzo-lactic acid* ($HO,C_{20}H_9O_7$), by heating the two acids together to about 360°. It is analogous in properties to its homologue benzoglycolic acid.

2. *Essence of Cumin.—Cuminic Series.*

(1254) *Hydride of Cumyl; Essence of Cumin* ($C_{20}H_{11}O_2,H=148$): *Sp. gr. of vapour* 5·24; *Boiling pt.* 428°.—The essential oil obtained by distilling the seeds of the *Cuminum cyminum* with water consists of a mixture of hydride of cumyl and of a hydrocarbon ($C_{20}H_{14}$) termed cymol. The hydrocarbon is homologous with benzol (the hydrocarbon obtained by the distillation of dry benzoate of lime), and the oxidized portion is homologous with hydride of benzoyl. Hydride of cumyl is isomeric with essence of aniseed and of fennel.

The two components of the oil of cumin may be readily separated by agitating this oil with a moderately concentrated solution of bisulphite of soda: a crystalline compound is thus formed which yields the pure hydride of cumyl when heated with a solution of potash and submitted to distillation.

Hydride of cumyl may be distilled unaltered in vessels from which air is excluded, but if exposed to the air it quickly absorbs oxygen and becomes brown, producing cuminic acid and a resinous compound. Oxidizing agents, such as nitric and chloric acids, also convert the hydride of cumyl into cuminic acid: if it be treated with hydrate of potash, cuminate of potash is produced, whilst hydrogen is liberated.

(1255) *Cuminic acid* ($HO,C_{20}H_{11}O_3=9+155$) may be prepared by decomposing cuminate of potash with hydrochloric acid. It crystallizes in colourless plates which emit an odour resembling that of the common bug (*cimex lectularius*). Cuminic acid is fusible, and may be distilled unaltered at about 500°. It is sparingly soluble in water, but freely so in alcohol and in ether. Fuming nitric acid converts it into nitro-cuminic acid. If distilled with an excess of caustic baryta it yields a hydrocarbon ($C_{18}H_{12}$) termed *cumol*, which is homologous with benzol. *Cuminic anhydride* may be obtained by decomposing dry cuminate of soda with oxychloride of phosphorus.

The cuminates are monobasic; *cuminate of baryta* ($BaO, C_{20}H_{11}O_3$) forms beautiful iridescent plates: *cuminate of silver* is white, insoluble, and anhydrous; it speedily blackens by exposure to light.

(1256) *Cuminic alcohol* ($C_{20}H_{13}O,HO$; *Boiling pt.* about 470° Kraut) may be obtained by treating the essence with an alcoholic solution of potash in the manner directed for preparing benzoic alcohol (1248). It is a colourless oily liquid of an aromatic odour and burning taste: it may be distilled unchanged. It does not absorb oxygen when exposed to the air. When heated with hydrate of potash it yields cymol and cuminic acid. It does not form a colligated acid with sulphuric acid. Cuminic alcohol is isomeric with the oxidized component of oil of thyme.

(1257) *Cumylide of Cumyl*, or *Cumyl* ($(C_{20}H_{11}O_2)_2$.—When hydride of cumyl is treated with potassium, hydrogen is evolved, and *cumylide of potassium* ($C_{20}H_{11}O_2,K$) is formed, constituting a gelatinous mass, 1 molecule of which rapidly absorbs 4 atoms of oxygen from the air, and is converted into cuminate of potash. Water decomposes it into hydrate of potash and hydride of cumyl. When the cumylide of potassium is heated with chloride of cumyl, mutual decomposition occurs, and cumylide of cumyl is formed:—

$$\overbrace{C_{20}H_{11}O_2,K}^{\text{Cumylide of potassium.}}+\overbrace{C_{20}H_{11}O_2,Cl}^{\text{Chloride of cumyl.}}=KCl+\overbrace{C_{20}H_{11}O_2,C_{20}H_{11}O_2}^{\text{Cumylide of cumyl.}}.$$

Cumyl may be obtained from the result of this reaction by treating the mass first with a weak solution of potash, in order to convert any undecomposed essence of cumin into cuminate of potash; and then agitating it with ether; the supernatant ethereal layer which contains the cumyl in solution is dried over chloride of calcium, and heated gently to expel the ether, when pure cumyl is left. Cumyl presents the appearance of a viscous oil which is heavier than water; when gently heated it emits an agreeable odour like that of the geranium. It is freely soluble in boiling alcohol, and cannot be distilled without undergoing decomposition; hydrate of potash converts it into cuminate of potash, whilst a portion of oil of cumin is simultaneously produced:—

$$\overbrace{C_{20}H_{11}O_2,C_{20}H_{11}O_2}^{\text{Cumyl.}}+KO,HO=\overbrace{C_{20}H_{11}O_2,H}^{\text{Hydride of cumyl.}}+\overbrace{KO,C_{20}H_{11}O_3}^{\text{Cuminate of potash.}}.$$

(1258) *Chloride of Cumyl* or *Cuminic oxychloride* ($C_{20}H_{11}O_2,Cl$ $=182·5$): *Sp. gr.* 1·070; *Boiling pt.* about 495°.—This is a colourless mobile liquid which is obtained by distilling cuminic acid with perchloride of phosphorus.

Many other compounds of the cuminic series may be formed, analogous to those of the benzoic series which have been already described.

The homologous oils, $C_{16}H_7O_2,H$, and $C_{18}H_9O_2,H$, intermediate between hydride of benzoyl and hydride of cumyl, have not as yet been discovered, but the acid corresponding to the first of these, the *toluic* (or toluylic), is known. It may be procured by oxidizing cymol by long-continued boiling with nitric acid which has been diluted with about six times its bulk of water; and it is probable that by Piria's process of treating the lime-salt of this acid with formiate of lime (*note*, p. 542), the aldehyd (or the missing hydride), $C_{16}H_7O_2,H$, would be obtained.

3. *Essence of Cinnamon.—Cinnamic Series.*

(1259) *Oil of Cinnamon: Hydride of Cinnamyl* ($C_{18}H_7O_2,H$ *$=132$*).—Essence of cinnamon and essence of cassia consist chiefly of hydride of cinnamyl, with a small proportion of a hydrocarbon isomeric with oil of turpentine. The commercial essence has a sp. gr. varying between 1·025 and 1·05. It boils at from 430° to 445°. Hydride of cinnamyl is readily obtained in a state of purity by agitating the crude essence with a solution of bisulphite of potash. The crystalline product thus obtained must be pressed, washed with cold alcohol, and dried; after which it it must be dissolved at a gentle heat in dilute sulphuric acid: the hydride of cinnamyl then collects upon the surface of the liquid in the form of a colourless fragrant oil. This oil is slightly heavier than water; it absorbs oxygen rapidly from the air and becomes yellow, owing to the formation of a solid resin, mixed with cinnamic acid. Nitric acid combines with the hydride, and converts it into a solid mass of crystals. This compound is immediately decomposed by water into nitric acid and free hydride of cinnamyl. Dumas made use of this fact in separating the hydride from its associated hydrocarbon.

If hydride of cinnamyl be boiled with nitric acid, abundance of hydride of benzoyl is evolved, and benzoic acid is found in the solution. If the essence be boiled with chloride of lime, benzoate of lime is produced. Chiozza has also made the interesting observation that hydride of benzoyl may be converted into oil of cinnamon by dissolving the pure hydride of benzoyl in aldehyd, and saturating the mixture with hydrochloric acid gas: on the application of a gentle heat the liquid becomes brown; and on afterwards proceeding to distillation, oil of bitter almonds first passes over, and then oil of cinnamon. Oil of cinnamon may, in fact, be regarded as hydride of benzoyl in which an atom of hydrogen has been displaced by an equivalent of the hydrocarbon (C_4H_3), in which case the reaction in the foregoing experiment might be thus represented; water being eliminated under the influence of the hydrochloric acid, which is not indicated in the equation:—

$$\overbrace{C_{14}H_5O_2,H}^{\text{Hydride of benzoyl.}}+\overbrace{C_4H_3O_2,H}^{\text{Aldehyd.}}=\overbrace{C_{14}H_4(C_4H_3)O_2,H}^{\text{Hydride of cinnamyl.}}+H_2O_2.$$

With ammonia the oil of cinnamon forms a crystalline solid termed *cinnhydramide*, which is analogous to hydrobenzamide:—

$$3\,\overbrace{(C_{18}H_7O_2,H)}^{\text{Hydride of cinnamyl.}}+2\,H_3N=\overbrace{C_{54}H_{24}N_2}^{\text{Cinnhydramide.}}+3\,H_2O_2.$$

Several chlorinated substitution-compounds may be obtained from oil of cinnamon: one of these, *chlorocinnose* ($C_{18}H_3Cl_4O_2,H$), crystallizes in white needles, which are fusible, and may be volatilized without decomposition.

(1260) *Cinnamic Acid* ($HO,C_{18}H_{7}O_{3}=9+139$).—When hydride of cinnamyl is heated with hydrate of potash, hydrogen is evolved, and cinnamate of potash is formed :—

$$\overbrace{C_{18}H_{8}O_{2}}^{\text{Hydride of cinnamyl.}}+KO,HO=\overbrace{KO,C_{18}H_{7}O_{3}}^{\text{Cinnamate of potash.}}+H_{2}.$$

This acid is contained in many balsams, such as those of storax, of tolu, and of Peru; and it is sometimes deposited in old specimens of essence of cinnamon. It may be extracted from storax and from balsam of tolu after distilling off the portion which can be volatilized by distillation with water, by treating the residue with a weak solution of carbonate of soda; the acid may be precipitated from the impure cinnamate of soda by the addition of hydrochloric acid.

Pure cinnamic acid is soluble in boiling water, from which it crystallizes in brilliant plates. Alcohol dissolves it with facility. It fuses at 264°, and at 560° it enters into ebullition, and may be distilled unaltered.

Nitric acid converts it into *nitro-cinnamic* acid ($HO,C_{18}H_{6},NO_{4},O_{3}$) if care be taken to avoid heating the mass; otherwise it is decomposed, and hydride of benzoyl is formed, which is converted, by continuing the action, into benzoic and nitro-benzoic acids. If cinnamic acid be distilled with bichromate of potash and sulphuric acid it yields hydride of benzoyl. When fused with an excess of hydrate of potash it is resolved into acetic and benzoic acids, whilst hydrogen is liberated :—

$$\overbrace{HO,C_{18}H_{7}O_{3}}^{\text{Cinnamic acid.}}+2\,(KO,HO)=\overbrace{KO,C_{4}H_{3}O_{3}}^{\text{Acetate of potash.}}+\overbrace{KO,C_{14}H_{5}O_{3}}^{\text{Benzoate of potash.}}+H_{2}.$$

These reactions clearly indicate a close relation between cinnamic and benzoic acids: cinnamic acid may, in fact, be regarded as benzoic acid in which one atom of hydrogen has been displaced by ($C_{4}H_{3}$); thus $HO,C_{18}H_{7}O_{3}=HO,C_{14}H_{4}(C_{4}H_{3})O_{3}$; and Bertagnini has recently succeeded in converting oil of bitter almonds into cinnamic acid by heating the essence for some hours to 260° or 270° with an equivalent quantity of acetic oxychloride in a sealed tube. The reaction which occurs may be thus represented :—

$$\overbrace{C_{4}H_{3}O_{2},Cl}^{\substack{\text{Acetic}\\\text{oxychloride.}}}+\overbrace{C_{14}H_{5}O_{2},H}^{\substack{\text{Hydride of}\\\text{benzoyl.}}}=HCl+\overbrace{HO,C_{18}H_{7}O_{3}}^{\text{Cinnamic acid.}}.$$

The cinnamates are monobasic salts; those of the alkalies are readily soluble and are crystallizable. A solution of these salts gives a yellow precipitate with the persalts of iron.

If cinnamic acid be intimately mixed with four times its weight of caustic baryta and distilled, it loses carbonic acid, and becomes converted into cinnamol, a hydrocarbon which bears the same relation to the cinnamic series that benzol does to the benzoic:—

$$\overbrace{HO,C_{18}H_7O_3}^{\text{Cinnamic acid.}} + 2\,BaO = \overbrace{C_{16}H_8}^{\text{Cinnamol.}} + 2\,BaO,C_2O_4.$$

When cinnamic acid is distilled with perchloride of phosphorus it yields a compound corresponding to chloride of benzoyl. It may be termed *chloride of cinnamyl*, or *cinnamic oxychloride* ($C_{18}H_7O_2,Cl$).

(1261) *Styrone; Peruvine; Cinnamic Alcohol* ($HO,C_{18}H_9O$).—This substance is procured by the distillation of styracin, or metacinnamene ($C_{36}H_{16}O_4$; 1263) with a concentrated solution of potash or of soda: a milky liquid passes over, from which on saturating it with common salt a whitish cream rises to the surface, and gradually solidifies. According to Toel, cinnamic alcohol may be obtained in beautiful silky needles, which have an agreeable odour of hyacinths: it fuses at 91°, and may be distilled unaltered. Nitric acid liberates hydride of benzoyl from it.

No ethers corresponding to this supposed alcohol have as yet been obtained. When exposed to the action of atmospheric air under the influence of platinum black, it yields oil of cinnamon, the aldehyd of this alcohol (Strecker).

(1262) The *Storax* from which the preceding compound is obtained is a gum-resin of the consistence of honey, and of a brownish-grey colour; it has a powerful oppressive odour, and an aromatic taste; it consists of a mixture of styracin, of cinnamic acid, of a peculiar resin, and of styrol, which is an essential oil isomeric with cinnamol.

Styrol ($C_{16}H_8$; *Sp. gr. of liquid* 0·924) is distinguished from cinnamol by the remarkable change which it experiences on the application of a temperature of about 400°, when it becomes converted into a polymeric solid termed *metastyrol*, or *draconyl*. In order to obtain styrol, three parts of storax, and one of carbonate of soda, should be subjected to distillation with water: the alkali retains the cinnamic acid, and the styrol passes over. It may be distilled at 294°; but during this operation the residue in the retort is apt suddenly to rise in temperature, and to be converted into metastyrol. Styrol also comes over mixed with toluol, when the resin termed dragon's-blood (from the *Dracæna* *draco*) is submitted to distillation. Styrol is a very mobile, colourless oil, endowed with an aromatic persistent odour, recalling that both of benzol and of naphthalin. When treated with bichromate of potash and dilute sulphuric acid, styrol is converted into benzoic acid.

Metastyrol is polymeric with styrol and with cinnamol; it is a colourless solid of high refracting power, and is destitute both of smell and taste. It softens on the application of heat, and may be drawn out into threads. It is insoluble in water and in alcohol, and is but very sparingly soluble in ether. When subjected to a high temperature it may be distilled, and is re-converted into styrol; and this liquid may be again reduced to the solid form of metastyrol by heating it to 400° in a sealed tube.

(1263) Two other balsams, closely resembling storax, are also met with as articles of commerce, viz., the balsams of Peru and of tolu.

Balsam of Peru is a fragrant resin produced by several species of leguminous plants of the genus *Myrospermum*. It is sold in the form either of a hard resin, or of a black, semi-solid body, which contains a peculiar resin and two other closely related substances, viz. *cinnamic acid*, and *metacinnamene*, or *styracin*.

Styracin ($C_{36}H_{16}O_4$) is a crystallizable solid, which is freely soluble in alcohol and in ether; it is polymeric with hydride of cinnamyl: it fuses at 111°. When treated with potash it undergoes a change analogous to saponification, and furnishes cinnamic acid and styrone:—

$$\overbrace{C_{36}H_{16}O_4}^{\text{Styracin.}}+KO,HO=\overbrace{KO,C_{18}H_7O_3}^{\text{Cinnam. potash.}}+\overbrace{C_{18}H_{10}O_2}^{\text{Styrone.}}.$$

Balsam of Tolu is stated to be the produce of the *Myrospermum toluiferum*. It is met with in commerce in the form either of a rusty brown, semi-transparent resin, or in that of a soft, dark-coloured, transparent balsam, of the consistence of turpentine, with a remarkably fragrant and agreeable odour. It is composed of the same substances as the balsam of Peru, but the proportion of styracin is much smaller. The solid resinous portion, according to E. Kopp, consists of two resins which have the composition of hydrated oxides of styracin: styracin being $C_{36}H_{16}O_4$; resin α being 2 $HO,C_{36}H_{16}O_6$; and resin β, 4 $HO,C_{36}H_{16}O_6$. When balsam of tolu is distilled, it yields benzoic ether, and a hydrocarbon ($C_{14}H_8$) termed *toluol*.

4. *Oil of Spiræa—Salicylic Series.*

(1264) *Hydride of* Salicyl; Salicylous *Acid* ($H,C_{14}H_5O_4=122$):

Sp. gr. of liquid 1·173; *of vapour* 4·276; *Boiling pt.* 360°.—When the flowers of the meadow-sweet (*Spiræa ulmaria*) are distilled with water they yield an essential oil which consists chiefly of a fragrant compound termed *hydride of salicyl*, but which also contains a small quantity of a hydrocarbon isomeric with oil of turpentine, and a crystalline substance analogous to camphor. If the essence be agitated with a solution of potash, the hydride of salicyl is dissolved, and can afterwards be separated by the addition of an acid. It is, however, generally obtained by the decomposition of salicin (1271) by means of bichromate of potash: 2 parts of salicin and 2 of bichromate of potash are to be mixed with 16 parts of water in a retort, and 3 parts of oil of vitriol diluted with 8 of water are to be added; a slight reaction commences, attended with extrication of heat, and a sparing disengagement of gas: as soon as this has ceased a gentle heat may be applied, and oil of spiræa passes over and collects in the receiver in the form of a heavy oil. Carbonic and formic acids are produced at the same time, whilst sulphate of chromium remains in the retort. 25 parts of salicin yield about 6 of the essence.*

Hydride of salicyl is a colourless oil, which by exposure to the air speedily assumes a more or less intense red tint. It becomes solid at −4°. Hydride of salicyl is probably the aldehyd of salicylic acid, but it possesses the properties of an acid; it decomposes the carbonates with effervescence, and yields crystallizable salts. It forms with potash and soda both neutral and acid salts, which are permanent when dry, but when moist they undergo spontaneous decomposition, and become black. The neutral potash salt ($K,C_{14}H_5O_4+2\,Aq$) is soluble in alcohol. The acid salt ($K,C_{14}H_5O_4+H,C_{14}H_5O_4$) is sparingly soluble in water, but crystallizes from boiling alcohol in groups of delicate needles. A solution of salicylide of potassium gives yellow insoluble precipitates with the salts of baryta, manganese, lead, silver, and with the salts of both the oxides of mercury; salicylide of copper is of a green colour; but the most characteristic reaction of hydride of salicyl is the production of an intense violet colour with the persalts of iron, which gradually disappears on exposure to the air.

Ammonia transforms hydride of salicyl into *salhydramide*, $C_{42}H_{18}N_2O_6$ (1168).

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* Büchner states that the unexpanded flower-buds of the meadow-sweet contain salicin, and this substance, during flowering, by exposure to the air, absorbs oxygen, and thus *furnishes* hydride of salicyl.

(1265) *Hydride of Chloro-salicyl,* or *Chlorosalicylous Acid* ($H,C_{14}H_4ClO_4$).—This substance was formerly termed chloride of salicyl,* but its reactions show that it is more correctly regarded as salicylous acid in which an atom of hydrogen has been displaced by chlorine. It is procured by transmitting a current of dry chlorine gas through oil of spiræa, gently heated: copious evolution of hydrochloric acid ensues, and as soon as this ceases to be evolved the transformation is complete; on allowing the mass to cool, the compound crystallizes. It may be dissolved in boiling alcohol, which deposits it on cooling in colourless, rectangular, glistening plates. It melts at a gentle heat, and may be sublimed without decomposition. This substance is insoluble in water, but soluble in ether and in oil of vitriol. The alkalies dissolve it and form crystallizable salts. The chloro-salicylide of barium ($Ba,C_{14}H_4ClO_4+Aq$) forms a yellow, crystalline, sparingly soluble powder. Dry ammonia is rapidly absorbed by chlorosalicylous acid, forming a yellow resinous-looking compound termed *chlorosamide.* It is soluble in hot ether and crystallizes on cooling.

Corresponding compounds may be obtained, which contain respectively an atom of bromine and one of peroxide of nitrogen, in the place of the equivalent of chlorine. These bodies likewise combine with the alkalies and form crystallizable salts.

(1266) It will be observed that hydride of salicyl is metameric with benzoic acid. It is, however, supposed to be formed by the union of hydrogen with a peculiar radicle, termed ***salicyl*** ($C_{14}H_5O_4$), which contains 2 atoms more of oxygen than benzoyl. Although salicyl has not been isolated, yet a compound of salicyl with benzoyl, ***salicylide of benzoyl*** ($C_{14}H_5O_2,C_{14}H_5O_4$) is known; this substance may be procured by the action of chloride of benzoyl on hydride of salicyl (Cahours):—

$$\overbrace{\left.\begin{matrix}C_{14}H_5O_4\\H\end{matrix}\right\}}^{\text{Hydr. salicyl.}}+\overbrace{\left.\begin{matrix}C_{14}H_5O_2\\Cl\end{matrix}\right\}}^{\text{Chlor. benzoyl.}}=\overbrace{\left.\begin{matrix}C_{14}H_5O_4\\C_{14}H_5O_2\end{matrix}\right\}}^{\text{Salicyl. benzoyl.}}+\left.\begin{matrix}H\\Cl\end{matrix}\right\}.$$

It is a yellow crystalline solid which fuses at 260°, and may be sublimed at about 356°. It is identical with the ***parasalicyl*** of Ettling, obtained by the distillation of salicylide of copper.

If hydride of salicyl be fused with hydrate of potash, hydrogen is liberated, and salicylic acid is formed, which stands in the ion to hydride of salicyl that benzoic acid does to benzoyl, so that hydride of salicyl would be the aldehyd acid; thus:—

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* Gerhardt has obtained a compound which appears to be the true *chloride of salicyl* ($C_{14}H_5O_4,Cl$) by the action of perchloride of phosphorus on oil of winter-green. It is a fuming, slightly coloured liquid, which evolves heat when mixed with water, whilst the chloride is converted into salicylic and hydrochloric acids; $C_{14}H_5O_4Cl+H_2O_2=HO,C_{14}H_5O_5+HCl$.

$$\underbrace{H,C_{14}H_5O_4}_{\text{Hydride of salicyl.}}+KO,HO=\underbrace{KO,C_{14}H_5O_5}_{\text{Salicylate of potash.}}+H_2.$$

ollowing table gives a synoptic view of the principal s related to the oil of spiræa, embracing the compounds cyl series:—

icyl).	$H,C_{14}H_5O_4$
asium	$K,C_{14}H_5O_4+2\,Aq$
o.	$K,C_{14}H_5O_4+H,C_{14}H_5O_4$
oro- .	$H,C_{14}H_4ClO_4$
of .	$Ba,C_{14}H_4ClO_4+Aq$
mo- .	$H,C_{14}H_4BrO_4$
tro- .	$H,C_{14}H_4,NO_4,O_4$
yl .	$Cl,C_{14}H_5O_4$
zoyl .	$C_{14}H_5O_2,C_{14}H_5O_4$
ide .	$C_{14}H_5O_2,C_{14}H_5O_5$
. .	$C_{28}H_8O_8$
. .	$HO,C_{14}H_5O_5$
ash .	$KO,C_{14}H_5O_5+Aq$
per .	$KO,C_{14}H_4CuO_5+2\,Aq$
Ani- .	$HO,C_{14}H_4,NO_4,O_5$
do. .	$HO,C_{14}H_3(NO_4)_2O_5$
o. .	$HO,C_{14}H_4ClO_5$
do. .	$HO,C_{14}H_3Cl_2O_5$

Oil of winter-green (Salicylate of methyl or Gaultheric acid)	$C_2H_3O,C_{14}H_5O_5$ or $HO,C_{14}H_4(C_2H_3)O_5$
Gaultherate of potash	$KO,C_{14}H_4(C_2H_3)O_5$
Gaultherate of methyl	$C_2H_3O,C_{14}H_4(C_2H_3)O_5$
Salhydramide . .	$C_{42}H_{18}N_2O_6$
Thiosalicol . . .	$C_{14}H_6O_2S_2$
Salicin	$C_{26}H_{18}O_{14}$
Chlorosalicin . .	$C_{26}H_{17}ClO_{14}+4\,Aq$
Dichlorosalicin . .	$C_{26}H_{16}Cl_2O_{14}+2\,Aq$
Trichlorosalicin . .	$C_{26}H_{15}Cl_3O_{14}+2\,Aq$
Helicin	$2\,(C_{26}H_{16}O_{14})+3\,Aq$
Helicoidin . . .	$C_{26}H_{18}O_{14},C_{26}H_{16}O_{14}+3\,Aq$
Saligenin	$C_{14}H_8O_4$
Chlorosaligenin . .	$C_{14}H_7ClO_4$
Dichlorosaligenin .	$C_{14}H_6Cl_2O_4$
Trichlorosaligenin .	$C_{14}H_5Cl_3O_4$
Saliretin	$C_{14}H_6O_2$
Populin or Benzoyl-salicin . .	$C_{40}H_{22}O_{16}+4\,Aq$; or $C_{26}H_{17}(C_{14}H_5O_2)O_{14}+4\,Aq$
Benzoyl-helicin . .	$C_{26}H_{15}(C_{14}H_5O_2)O_{14}$
Coumarin . . .	$C_{18}H_6O_4$

) *Salicylic Acid* ($HO,C_{14}H_5O_5=9+129$).—This comy be obtained also by mixing 1 part of salicin with a ted solution of 3 parts of hydrate of potash in a silver and fusing the mass, continuing the heat until the ecomes white, taking care not to allow the temperature yond 750°. On adding hydrochloric acid to the mass as been dissolved in water, salicylic acid is precipitated. is also readily prepared from the oil of winter-green, g it for a few minutes with a solution of caustic in this operation wood spirit is liberated, and on the of an acid, salicylic acid is precipitated. Coumarin so yields this acid when exposed to similar treatment. wise obtained by decomposing anthranilic acid (1327) ns acid.

lic acid is sparingly soluble in cold water, but is readily by boiling water, from which it crystallizes on cooling in long slender needles. It fuses at 316°, and if pure, may at a higher temperature be sublimed unaltered. When salicylic acid is distilled with an excess of lime, it yields carbonic and phenic (carbolic) acids:—

$$\overbrace{HO,C_{14}H_5O_5}^{\text{Salicylic acid.}} + 2\,CaO = 2\,CaO,C_2O_4 + \overbrace{HO,C_{12}H_5O.}^{\text{Phenic acid.}}$$

The monobasic salicylates of the alkalies yield pure phenic acid on distillation; and Kolbe states that on transmitting a stream of carbonic acid into carbolic acid whilst it is dissolving sodium, the salicylate of the base is reproduced, whilst hydrogen escapes.

Salicylates. — Salicylic acid forms compounds which are in many respects anomalous. It is generally considered to be a monobasic acid, but it forms two distinct classes of salts, one of which contains one equivalent, the other two equivalents of base; the acid, therefore, has been represented by the formula $HO, C_{14}H_5O_5$, as well as by that of $2\ HO,C_{14}H_4O_4$. The monobasic salts may be preserved unaltered in a dry state, but they become brown if exposed to the air in a moist condition.

The soluble salicylates are characterized by the property which they possess, of forming an inky blue precipitate when mixed with solutions of the persalts of iron. This colour disappears on the addition of free hydrochloric acid. The anomalous character of the salicylates renders their constitution an object of considerable interest, and we shall therefore describe a few of these compounds.

The *monobasic salicylate of potash* ($KO,C_{14}H_5O_5+Aq$) crystallizes from its alcoholic solution in silky needles. Piria, (Liebig's *Annal.* xciii. 262), has obtained a double *salicylate of copper and potash* ($KO,C_{14}H_4Cu,O_5+4\ Aq$), which crystallizes in large emerald green plates. The ordinary *lime* salt ($CaO,C_{14}H_5O_5 + 2\ Aq$) is very soluble, and crystallizes in octohedra of great beauty. If a solution of this salt be mixed with a solution of lime in syrup, a *dibasic salicylate of lime* ($CaO,C_{14}H_4Ca,O_5+2\ Aq$), which is sparingly soluble in water, is deposited in hard crystalline grains. The aqueous solution of this salt has an alkaline reaction, and is decomposed by the action of carbonic acid, carbonate of lime being formed, and the monobasic lime salt being set free. A similar salt may be obtained with *baryta* ($BaO, C_{14}\left.\begin{matrix}H_4\\Ba\end{matrix}\right\}O_5+4\ Aq$); if heated to 212° it loses 4 atoms of water. With lead, salicylic acid forms three distinct compounds: the *monobasic salicylate of lead* ($PbO,C_{14}H_5O_5+Aq$) is a sparingly soluble salt, which is crystalline and has a silky lustre. If tribasic acetate of lead be added to a boiling solution of this salt, a *dibasic*

late of lead is deposited as a heavy, white, crystalline, an-
us powder ($PbO,C_{14}\left.\begin{matrix}H_4\\Pb\end{matrix}\right\}O_5$; but if the solution of the mono-
salt be decomposed by adding an excess of ammonia, instead
e tribasic acetate of lead, the liquid when boiled deposits a
basic lead salt ($4\,PbO,C_{14}\left.\begin{matrix}H_4\\Pb\end{matrix}\right\}O_6$).

These anomalies may be explained by supposing that the
al salts of salicylic acid are monobasic, but that a second
of hydrogen in the radicle of the acid, in certain cases,
s of being displaced by a metal, thus giving rise to a series
lts which present the characters of basic salts.*

Gerhardt has found (*Ann. de Chimie*, III. xlv. 90) that this
d equivalent of hydrogen in the radicle is displaceable by
oyl, and other electro-negative groups. The mode of forming
e compounds will be best understood after the properties of the
ylate of methyl, or oil of wintergreen, have been described.

(1268) *Salicylate of Methyl; Oil of Wintergreen,* or *Gaultheric*
$[C_2H_3O,C_{14}H_5O_5=HO,C_{14}H_4(C_2H_3)O_5]$; *Sp. gr. of liquid*
; *of vapour* 5·42.—The flowers of the *Gaultheria procumbens*
h an essence consisting chiefly of salicylate of methyl, mixed
a small proportion of a hydrocarbon, termed *gaultherilene,*
ch is isomeric with oil of turpentine. This hydrocarbon boils
0°, and constitutes the more volatile portion of the essence;
alicylate of methyl is procured by collecting separately those
ons which come over after the boiling point has risen to 432°,
hich point it continues stationary. It may also be obtained
cially by distilling a mixture of 2 parts of crystallized salicylic
, 2 of anhydrous wood spirit, and 1 part of oil of vitriol.

In whichever mode it is obtained it presents the appearance of
ourless or yellowish oil, of a powerful, agreeable, and per-
nt odour. It is sparingly soluble in water, and its aqueous
tion acquires a violet tint when mixed with a persalt of iron.
ral substitution products, containing chlorine, bromine, and
ide of nitrogen, may be obtained from the essence.

It is probably like lactic acid a monobasic acid on the diatomic type
(1136):—

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_4 \quad ; \quad \overbrace{\left.\begin{matrix}(C_{14}H_4O_2)''\\H,H\end{matrix}\right\}O_4}^{\text{Salicylic acid.}}.$$

alicylic acid in solution is treated with amalgam of sodium, a new
lylic, is formed; it is metameric with the benzoic, and stands in the
n to salicylic acid that propionic does to lactic acid, containing 2
gen less.

long slender needles. It fuses at 316°, and if [illegible]
temperature be sublimed unaltered. When [illegible]
with an excess of lime, it yields carbonic and [illegible]

$$\overbrace{HO,C_{14}H_5O_5}^{\text{Salicylic acid.}}+2\,CaO=2\,CaO,C_2O\ldots$$

The monobasic salicylates of the alkalies [illegible]
distillation; and Kolbe states that on [illegible]
carbonic acid into carbolic acid whilst [illegible]
salicylate of the base is reproduced, [illegible]

Salicylates. — Salicylic acid for [illegible]
many respects anomalous. It is [illegible]
monobasic acid, but it forms two [illegible]
which contains one equivalent, the [illegible] of lea
the acid, therefore, has been re [illegible] precipita
$C_{14}H_5O_5$, as well as by that of [illegible] —The other e
salts may be preserved unaltered [illegible] acids, and Cah
brown if exposed to the air in [illegible] may be again eth

The soluble salicylates are [illegible] $H_2O,C_{14}H_4(C_2H_3)O_4]$
they possess, of forming an in [illegible] corresponds exactly
solutions of the persalts of [illegible] dibasic lead salt, for
addition of free hydrochlori [illegible] alicylic ethers may
the salicylates renders th [illegible] substitution-compounds,
derable interest, and we [illegible] ers is anomalous. In
compounds. [illegible] the ethylic or methylic

The *monobasic salic* [illegible] in the salicylic ethers,
tallizes from its alco [illegible] periences the displacement
(Liebig's *Annal.* xciii [illegible] in the reaction is the form
of copper and potash [illegible]
in large emerald gre [illegible] arising partially out of the
+ 2 Aq) is very sol [illegible] the formation of ethers
beauty. If a solut [illegible] of ethyl should act the pa
lime in syrup, a *dib* [illegible] taining compounds corres
which is sparingly [illegible] of benzoyl be made to
line grains. The [illegible] is obtained, termed *ben*
reaction, and is [illegible] $C_{14}H_4O_3$), which crystall
bonate of lime [illegible]
set free. A [illegible]

$$C_{14}\left.\begin{matrix}H_4\\Ba\end{matrix}\right\}O_5+4\ \ldots = \overbrace{\left.\begin{matrix}C_{14}H_4(C_2H_3)O_4\\C_{14}H_5O_2\end{matrix}\right\}}^{\text{Benzoate of methyl-salicyl.}}O_2+\ldots$$

With lead, [illegible] of a dibasic acid, such
monobasic [illegible] *succinate of methyl-salicyl* [
soluble salt, [illegible] formed, and obtained crystallized
acetate of [illegible] rectangular plates.

(1270) *Salicylic anhydride* ($C_{14}H_5O_5,C_{14}H_5O_5$) may be procured by the action of oxychloride of phosphorus on dry salicylate of soda; at the same time a quantity of *salicylide* ($C_{28}H_8O_8$) is produced. The latter body is analogous to lactide (1138); it contains two atoms of water less than are present in salicylic anhydride. Both salicylide and salicylic anhydride are rapidly converted into ordinary salicylic acid, when heated with a solution of potash.

When salicylic acid is swallowed, a portion of it finds its way into the urine, but it becomes converted into a crystallizable colligated combination of glycocine, termed *salicyluric acid* $HO,C_{18}H_8NO_7$) by a process analogous to that which converts benzoic acid, under similar circumstances, into hippuric acid. The solutions of salicyluric acid give a violet colour with persalts of iron. When boiled with concentrated hydrochloric acid, salicyluric acid is split up into salicylic acid and glycocine.

Portions of the hydrogen in salicylic acid may be displaced by chlorine and by bromine, forming *chlorosalicylic* and *dichlorosalicylic, bromosalicylic* and *dibromosalicylic* acids. A mixture of hydrochloric acid and chlorate of potash converts salicylic acid into chloranile (perchloroquinone) $C_{12}Cl_4O_4$.

Fuming nitric acid converts the salicylic into *nitro-salicylic* (indigotic or anilic) acid, ($HO,C_{14}H_4,NO_4,O_5$), and by prolonged digestion with it furnishes carbazotic acid [$HO,C_{12}H_2(NO_4)_3O$]. Nitrosalicylic acid may also be obtained by adding indigo in small quantities at a time to boiling nitric acid, which has been previously diluted with ten or twelve parts water: as the liquid cools the acid crystallizes. It is sparingly soluble in cold water, but freely so in boiling water and in alcohol: it fuses easily, and may be sublimed unaltered at a gentle heat. Its solutions when mixed with the persalts of iron give a red colour. With salts of lead it gives a pale yellow voluminous precipitate ($PbO, C_{14}H_4NO_4,O_5+Aq$). The salts of potash and of ammonia may be obtained in orange-coloured silky needles. A *dinitrosalicylic acid* [$HO,C_{14}H_3(NO_4)_2O_5$] may also be formed.

(1271) SALICIN ($C_{26}H_{18}O_{14}=286$).—This substance has been made the subject of a series of interesting researches by Piria (*Ann. de Chimie,* II. lxix. 281, and III. xiv. 257). Salicin is contained in the bark of most of the willows, and confers upon them their peculiar bitterness. It is procured by adding to an aqueous infusion of the bark, hydrated oxide of lead, by which the tannin and colouring matters are removed, and then on filtering and evaporating the liquid the salicin is obtained in crystals. It is soluble in five or six parts of cold wate is still more readily dissolved by alcohol. These so exert a left-handed rotatory action upon a ray of p light. A solution of salicin is not precipitated by infu gelatin, nor by one of tannin, but with an ammoniacal s of acetate of lead it yields a precipitate consisting of $C_{26}H_{1}$ When salicin is moistened with strong sulphuric acid it a a deep red colour, and a compound acid is formed which h termed *sulpho-rufic* acid.

When salicin is boiled for a few minutes with dilute su or hydrochloric acid a remarkable change occurs; grape found in the solution, and on neutralizing the acid, the strikes a very intense blue with the persalts of iron, owin presence of *saligenin* ($C_{14}H_8O_4$).* On agitating the soluti ether, the saligenin is separated, and may be obtained o ration crystallized in pearly tables, which fuse at 180°. A transformation is effected when salicin is allowed to stand time after mixture with a solution of synaptase (*note* The change which occurs may be thus represented:—

$$\overbrace{C_{26}H_{18}O_{14}}^{\text{Salicin.}} + 2\,H_2O_2 = \overbrace{C_{14}H_8O_4}^{\text{Saligenin.}} + \overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

By heating saligenin carefully in closed vessels two equ of water are expelled, and a resinous body named *saliretin* (C remains. The same effect is produced by boiling salicin genin for some time with a dilute acid; the solution turbid and deposits the resin, which is insoluble in wa soluble in alcohol, ether, and concentrated acetic acid. quires a red colour when moistened with oil of vitriol.

When salicin is heated to 248° it fuses, and at a high perature is completely decomposed. If heated with hy potash it is also decomposed, and oxalate and salicylate of are formed. Concentrated nitric acid converts salicin int and carbazotic acids. If salicin be boiled with sulphu and peroxide of manganese, formic acid is the principal But the most interesting transformation of which it is sus

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* *Phillyrin* ($C_{54}H_{34}O_{22}+3\,Aq$) is the name given to a crystalli stance contained in the bark of the *Phillyrea*, which splits, when bo acids, into grape sugar and a resinous substance; and which when to lactic fermentation yields *phillygenin* and sugar, phillygenin c the elements of 3 atoms of saligenin (Bertagnini).

$$\overbrace{C_{54}H_{34}O_{22}}^{\text{Phillyrin.}} + 2\,H_2O_2 = \overbrace{C_{42}H_{24}O_{12}}^{\text{Phillygenin.}} + \overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

is that produced by chromic acid:—if 1 part of salicin be mixed with 1 part of bichromate of potash, 1½ of sulphuric acid, and 20 parts of water, on the application of a gentle heat formic and carbonic acids are produced, whilst a fragrant oily liquid distils over with the vapour of water, and condenses in the receiver; it has exactly the odour of the meadow-sweet or the heliotrope, and analysis has proved it to have the same composition ($C_{14}H_6O_4$) as the essential oil of these plants. Both saligenin and saliretin also yield oil of spiræa when treated with bichromate of potash and sulphuric acid, the change effected being simply one of oxidation:—

$$\overbrace{2\,C_{14}H_8O_4}^{\text{Saligenin.}}+O_4=2\,\overbrace{(H,C_{14}H_5O_4)}^{\text{Oil of spiræa.}}+2\,H_2O_2;\ \text{and}$$

$$\overbrace{2\,C_{14}H_6O_2}^{\text{Saliretin.}}+O_4=2\,\overbrace{(H,C_{14}H_5O_4)}.$$

Chlorine produces three different substitution products with salicin; viz., $C_{26}H_{17}ClO_{14}$; $C_{26}H_{16}Cl_2O_{14}$; and $C_{26}H_{15}Cl_3O_{14}$. When digested with synaptase they each furnish a corresponding chlorinated form of saligenin (see table, p. 563), and if boiled with dilute acids each yields a corresponding chlorinated form of saliretin.

Helicin 2 $C_{26}H_{16}O_{14}+3$ Aq.—When one part of salicin is digested without the application of heat in 10 parts of nitric acid of sp. gr. 1·160 for twenty-four hours, it becomes gradually dissolved, and loses 2 equivalents of hydrogen; the solution acquires a yellow colour, and crystals of helicin are deposited: the mother liquor must be removed by submitting the crystals to pressure in linen, after which they must be washed with cold water and with ether, which leaves them in a state of purity. Helicin crystallizes in small delicate colourless needles, which are very soluble in boiling water and in alcohol, but not in ether. It has a bitterish taste; when heated to 212° it loses its water of crystallization; it fuses at 347°, and is gradually decomposed, becoming converted into an insoluble resinoid mass. Under the influence of alkalies, or of synaptase, helicin assimilates the elements of water and is converted into oil of spiræa, and glucose:—

$$\overbrace{C_{26}H_{16}O_{14}}^{\text{Helicin.}}+2\,H_2O_2=\overbrace{C_{14}H_6O_4}^{\text{Oil of spiræa.}}+\overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

Dilute nitric acid also decomposes helicin, and liberates oil of spiræa. When boiled with dilute nitric acid, nitrosalicylic and oxalic acids are formed.

Helicoidin ($C_{52}H_{34}O_{28}+3$ Aq$=C_{26}H_{18}O_{14},C_{26}H_{16}O_{14}+3$ Aq is a crystalline compound which is the result of the imperfect oxidation of salicin. It is prepared in the same manner as helicin, but the specific gravity of the nitric acid employed must not exceed 1·09. The circumstances necessary to ensure its production are, however, not accurately known.

Both chlorine and bromine form compounds with helicin, in which 1 atom of hydrogen is displaced by an equivalent of chlorine or of bromine, the formula of *chlorohelicin* being $C_{26}H_{15}ClO_{14}$: it is decomposed by synaptase into glucose and chloride of salicyl.

Nature of Salicin.—The foregoing observations and experiments appear to lead definitely to the conclusion that salicin must be regarded as a colligated body derived from saligenin and grape sugar. Saligenin is a substance which readily undergoes transformations by chemical agents, being converted by sulphuric acid into a peculiar red compound, by nitric acid into carbazotic acid, and by other oxidizing agents into oil of spiræa. When salicin is submitted to the action of chemical agents, the saligenin is the constituent which is first affected if these agents act with moderate intensity; whilst the sugar either remains in combination with the modified saligenin, as in the various forms of chlorosalicin, or it is set at liberty. If the reaction be more violent, the elements of the sugar also take part in the changes which are effected: for example, when salicin is oxidized by chromic acid, the saligenin yields the oil of spiræa, and the sugar produces formic acid.

(1272) *Populin* [$C_{40}H_{22}O_{16}+4\,Aq=C_{26}H_{17}(C_{14}H_5O_2)O_{14}+4\,Aq$].—This compound may be regarded as salicin, in which one atom of hydrogen has been displaced by benzoyl. It is found in the bark and the leaves of the aspen (*Populus tremula*), and probably also in other varieties of the poplar. It is extracted by a process similar to that employed for salicin. Populin requires about 70 parts of boiling water for its solution, and 2000 parts of cold water; it is freely soluble in boiling alcohol. When crystallized from a hot aqueous solution it forms colourless, silky, extremely delicate needles, which have a sweetish taste resembling that of liquorice; these crystals, if heated to 212°, lose 4 Aq.; at a higher temperature they are decomposed, benzoic acid being amongst the products. When boiled with baryta water for a few minutes, a clear solution is obtained, and on separating the excess of baryta by means of a current of carbonic acid, the solution is found to contain salicin and benzoate of baryta:—

$$\overbrace{C_{40}H_{22}O_{16}}^{\text{Populin.}}+HO,BaO=\overbrace{BaO,C_{14}H_5O_3}^{\text{Benzoate of baryta.}}+\overbrace{C_{26}H_{18}O_{14}}^{\text{Salicin.}}$$

n boiled with dilute acids populin is decomposed into a mix-
of benzoic acid, saliretin, and glucose :—

$$\overbrace{C_{40}H_{22}O_{16}}^{\text{Populin.}}+2\,H_2O_2=\overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}}+\overbrace{C_{14}H_6O_2}^{\text{Saliretin.}}+\overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

ptase is without action upon populin : concentrated nitric acid
erts it into a mixture of nitrobenzoic, carbazotic, and oxalic
; dilute nitric acid converts it into *benzoylhelicin*, $C_{26}H_{15}$
$I_4O_2)O_{14}$. A mixture of bichromate of potash and sulphuric
liberates oil of spiræa from populin in abundance.

(1273) *Coumarin* ($C_{18}H_6O_4=148$) ; *Fusing pt.* 122° ; *Boiling pt.*
—This substance is found in the Tonka bean (*Coumaroma*
ata), in the common melilot, in the sweet-scented vernal grass,
hich much of the fragrance of hay is owing, and in several
sweet-scented plants. Coumarin is most easily extracted from
Tonka bean by digesting the powdered seeds in alcohol ; on
rating the alcoholic solution, crystals of coumarin are ob-
ed, and may be purified by digestion with animal charcoal,
by recrystallization. Coumarin assumes the form of colour-
rectangular plates, or of rhombic prisms with slightly rounded
s. It may be distilled unaltered. Its vapour has an agree-
aromatic odour. It has a burning taste, and is but slightly
ble in cold water, though it is freely dissolved by boiling
r; the solution on cooling deposits coumarin in silky needles.
te acids dissolve it without alteration. Concentrated nitric
converts it at first into *nitrocoumarin* [$C_{18}H_5(NO_4)O_4$], but by
nged boiling it transforms it into carbazotic acid. Substi-
n compounds containing chlorine and bromine may also be
ed from it. One of its most singular compounds is obtained
ating coumarin with a solution of perchloride of antimony in
chloric acid : gas is evolved, and as the liquid cools, a canary-
w precipitate ($C_{18}H_6O_4,SbCl_3$) is deposited in crystals.

When coumarin is boiled with a concentrated solution of
ate of potash it assimilates the elements of water, and is con-
d into *coumaric acid*, which combines with the potash :—

$$\overbrace{C_{18}H_6O_4}^{\text{Coumarin.}}+KO,HO=\overbrace{KO,C_{18}H_7O_5}^{\text{Coumarate of potash.}}.$$

maric acid crystallizes in brilliant transparent plates, which
obtained by decomposing a hot solution of coumarate of
y hydrochloric acid. It fuses at about 374° ; at a higher
ure it is decomposed, yielding a crystalline sublimate, and
ich combines with potash, and reddens the persalts of iron.

When coumaric acid is fused with hydrate of potash, it is decomposed into acetate and salicylate of this base (Chiozza), whilst hydrogen escapes :—

$$\overbrace{HO,C_{18}H_7O_5}^{\text{Coumaric acid.}}+2\,(KO,HO)=\overbrace{KO,C_4H_3O_3}^{\text{Acetate of potash.}}+\overbrace{KO,C_{14}H_5O_5}^{\text{Salicylate of potash.}}+H_2.$$

5. *Oil of Aniseed.—Anisic Series.*

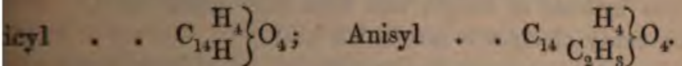
(1274) The essential oils furnished by the seeds of *Pimpinella anisum,* or common anise, of the *Anethum fœniculum,* or fennel, of the *Illicium anisatum,* or star anise, and of the *Artemisia dracunculus,* or tarragon, are closely allied to each other; they vary in odour, but all consist of two portions, one of which is a hydrocarbon isomeric with oil of turpentine, and the other is a solid crystalline oxidized compound ($C_{20}H_{12}O_2$), which is convertible by oxidation into hydride of anisyl ($C_{16}H_7O_4,H$).

Solid Essence of Aniseed ($C_{20}H_{12}O_2$); *Sp. gr. of solid* 1·014; *of vapour* 5·19; *Fusing pt.* 65°; *Boiling pt.* 432°.—The crude essence of aniseed contains nearly four-fifths of its weight of this oxidized compound; which may be separated by exposing the oil to a low temperature, submitting the magma to pressure between folds of filtering paper, and crystallizing the residue from hot alcohol (sp. gr. 0·850). This substance when treated with chlorine or with bromine yields substitution compounds.

When essence of aniseed is mixed with concentrated oil of vitriol it is dissolved, and a red solution is formed; on the addition of water, this solution is decomposed, and a substance termed *anisoine,* isomeric with the solid essence, is precipitated in white resinoid masses. A similar change is produced by treating the essence with bichloride of tin or with terchloride of antimony. This modification is insoluble in alcohol, but is soluble in ether and the essential oils: it is rather heavier than water, and is fusible above 212°. The oils of tarragon and of bitter fennel appear each to contain a distinct compound which is isomeric with anisoine and with the solid portion of oil of anise; the principal portion of essence of tarragon consisting of a modification which boils at 403°, and requires a low temperature for its solidification. These bodies, when oxidized, yield anisic acid, and other products which are identical with those furnished by oil of aniseed. Oil of cumin is also isomeric with the solid essence of anise, but the products of its oxidation are different (1254).

If oil of aniseed be heated in a sealed tube to 430°, in contact with a mixture of hydrate of soda and lime, a small quantity of d is formed, which is isomeric with cuminic acid, but not al with this compound.

e action of nitric acid upon oil of aniseed gives rise to a of compounds which have been particularly examined by rs. They present a close analogy with the compounds of licylic series. They may be regarded as containing a radicle l *anisyl* ($C_{16}H_7O_4$), which may be viewed either as a homo- of salicyl, or as a body in which one equivalent of hydrogen en displaced by an equivalent of methyl; thus—



$$\text{icyl} \quad . \quad . \quad C_{14}\left.\begin{matrix}H_4\\H\end{matrix}\right\}O_4; \qquad \text{Anisyl} \quad . \quad . \quad C_{14}\left.\begin{matrix}H_4\\C_2H_3\end{matrix}\right\}O_4.$$

he principal members of the anisic group are—

Hydride of anisyl	$C_{16}H_7O_4,H$
Anisylic alcohol	$C_{16}H_9O,HO$
Anisic acid	$HO,C_{16}H_7O_4,O$
Chloride of anisyl	$C_{16}H_7O_4,Cl$
Anisine	$C_{48}H_{24}N_2O_6$.

(1275) *Hydride of Anisyl* ($C_{16}H_7O_4,H$); *Sp. gr.* 1·09; *Boiling* bout 490°.—When oil of aniseed is acted upon by dilute c acid, a reddish oil is obtained, consisting of a mixture of c acid and hydride of anisyl. A quantity of oxalic acid is ys formed during its preparation, which may be explained by ollowing equation:—

$$\overbrace{C_{20}H_{12}O_2}^{\text{Essence of anise.}}+3\,O_4=\overbrace{C_{16}H_7O_4,H}^{\text{Hydride of anisyl.}}+2\,\overbrace{HO,C_4O_6}^{\text{Oxalic acid.}}+H_2O_2.$$

e oil thus obtained be washed with a weak solution of potash, der to remove anisic acid, and be then cautiously distilled, the ide passes over in the form of an amber-coloured liquid, which an aromatic odour resembling that of new hay. Hydride of yl is homologous with oil of spiræa. It is freely soluble in ol and in ether, but insoluble in water. Sulphuric acid lves it and forms a dark red liquid, from which on dilution water the oil is separated unaltered. Hydride of anisyl forms lline compounds with the bisulphites of the alkalies.

Anisylic Alcohol ($C_{16}H_9O,HO$); *Boiling pt.* about 480°.— le of anisyl be dissolved in an equal volume of alcohol ed with three times its volume of a solution of potash ·05) it is decomposed into anisic acid and anisylic alcohol. c acid crystallizes out as anisate of potash, whilst the ol remains in solution; it is decanted and distilled to

get rid of the ordinary alcohol; it is then mixed with eth
dissolves the anisylic alcohol, and leaves it on evaporati
yellowish oil. It may be distilled and freed from a
hydride of anisyl by digestion with a bisulphite of on
alkalies. On redistillation it is obtained as an oil which
when anhydrous at 73°, but if it contains water it cryst
a lower temperature in hard shining needles; it is heav
water, and has a feebly spirituous odour and a burni
Oxidizing agents, such as dilute nitric acid, gradually
it into hydride of anisyl, and then into anisic acid.
black easily changes it into anisic acid.

Ammonia converts the hydride of anisyl into *anishy*
$3\ C_{16}H_8O_4 + 2\ H_3N = C_{48}H_{24}N_2O_6 + 3\ H_2O_2$. If anishydr
maintained for two hours at a temperature of 330° o
fuses and becomes converted into an isomeric base, terme
This body is soluble in alcohol, but scarcely soluble in wa
ether. Its alcoholic solution has a strongly alkaline reacti
bitter taste; it deposits the alkali in colourless prisms.
of this base may be obtained in crystals.

(1276) *Anisic Acid* ($HO,C_{16}H_7O_5 = 9 + 143$).—This
is isomeric with salicylate of methyl, and has the compos
homologue of salicylic acid. It may be obtained by boili
anise with nitric acid (of sp. gr. 1·20); a yellow resinc
termed *nitraniside* [$C_{20}H_{10}(NO_4)_2O_2$] is thus formed, and t
on cooling deposits long, colourless brilliant prisms of an
This acid is scarcely soluble in cold water, but is freely s
boiling water, in alcohol, and in ether. It melts at 3
may be sublimed unaltered, condensing in white needles;
concentrated nitric acid converts it into *nitranisic aci*
$C_{16}H_6NO_4,O_5$). The anisates are monobasic; those of th
lies and of the earths are soluble and crystallizable: but
lead, silver, and mercury are insoluble in cold water.

Chloride of Anisyl ($C_{16}H_7O_4,Cl = 170·5$); *Sp. gr.* 1·2
colourless oil of a penetrating, powerful odour; it is proc
distilling anisic acid with perchloride of phosphorus.
at 504°.

(1277) *Anisol* ($C_{14}H_8O_2$); *Sp. gr.* 0·991; *Boiling pt.*
anisic acid be distilled with an excess of caustic baryta,
a compound termed *anisol*, or *phenomethol* :—

$$\overbrace{HO,C_{16}H_7O_5}^{\text{Anisic acid.}} + 2\ BaO = 2\ BaO,C_2O_4 + \overbrace{C_{14}H_8O_2}^{\text{Anisol.}}$$

Anisol has the composition of phenate of methyl (C_2H_3O,C

has obtained it synthetically by decomposing iodide of ith phenate of potash (1365) :—

$$\overbrace{C_2H_3I}^{\text{Iodide of methyl.}}+\overbrace{KO,C_{12}H_5O}^{\text{Phenate of potash.}}=KI+\overbrace{C_2H_3O,C_{12}H_5O}^{\text{Anisol.}}.$$

a colourless liquid of an aromatic odour; it is soluble in well as in alcohol and ether. When treated with fuming d, substitution compounds are obtained, which may con- , or 3 equivalents of peroxide of nitrogen. *Nitranisol* $)_{14}O_2)$, when treated with an alcoholic solution of hydro- of ammonia, yields a base termed *anisidine* ($C_{14}H_9NO_2$), phur is deposited; and if *dinitranisol* be similarly treated, base, *nitranisidine*, is obtained :—

$$\overbrace{{}_{14}H_6(NO_4)_2O_2}^{\text{Dinitranisol.}}+3\,H_2S_2=\overbrace{C_{14}H_8(NO_4)NO_2}^{\text{Nitranisidine.}}+2\,H_2O_2+3\,S_2.$$

dine crystallizes in long brilliant needles, which are of a brown colour: it forms well defined crystallizable salts phuric, nitric, and hydrochloric acids. If *trinitranisol* $NO_4)_3O_2]$ be treated with hydrosulphate of ammonia, it third base, *dinitranisidine* [$C_{14}H_7(NO_4)_2NO_2$], the salts of owever, are very unstable, and are decomposed by contact er. Nitranisidine when treated with the chlorides of benzoyl, nyl, and of cumyl yields new compounds, in which benzoyl, , and cumyl are substituted for hydrogen, and compounds s to benzamide are produced; for example :—

$$\overbrace{H_8NO_4,NO_2}^{\text{itranisidine.}}+\overbrace{C_{14}H_5O_2,Cl}^{\text{Chloride of benzoyl.}}=\overbrace{C_{14}H_7,C_{14}H_5O_2,NO_4NO_2}^{\text{Benzonitranisamide.}}+HCl.$$

nts of this nature present an interest in connexion with ion of the artificial formation of the natural organic bases; irical formula of benzonitranisamide ($C_{28}H_{12}N_2O_8$), pre- onsiderable resemblance to that of some of the natural

(C.) *Essential Oils which contain Sulphur.*

8) THE ALLYL SERIES.—The basis of all the oils of the tted essences which have been accurately examined is the bon termed allyl (C_6H_5). Oil of garlic is a mixture of ith sulphide of allyl; and the essences of onions and a, and many of the *Asphodeleæ* and *Cruciferæ*, yield similar essential oils of mustard, of horse-radish, and of scurvy sist chiefly of sulphocyanide of allyl.

allyl series has recently been invested with new interest bours of Berthelot and De Luca, who have succeeded in preparing the *iodide of allyl*, or iodized propylene, as they by decomposing glycerin with biniodide of phosphorus (discovery which in the hands of these chemists (*Comptes* Feb. 4, 1856), and in those of Hofmann and Cahours *Chimie*, III. l. 432) has led to the formation of numerou tives of allyl, and has demonstrated the intimate connexion compounds with acrolein and the products of its oxidation

(1279) *Allyl*, or *Allylide of Allyl* ($(C_6H_5)_2$; *Sp. gr.* 0·684; *of vapour* 2·92; *Boiling pt.* 138°.—When iodide o treated with sodium it is decomposed, iodide of sodium is and allyl is liberated in the form of a very volatile liquid, of a peculiar penetrating odour, resembling that of radish vapour burns with a very luminous flame. It is misc sulphuric acid, the mixture being attended with great ele temperature, and on standing for a few hours it gradually in a modified condition.

Allyl is immediately attacked by chlorine, brom iodine, with which it forms compounds to which the $C_6H_5Cl_2$; $C_6H_5Br_2$; and $C_6H_5I_2$, have been assigned. It ever, probable that these bodies are not true compounds with two equivalents of the halogen, but substitution perhaps of the form C_6H_4Cl,HCl, analogous to Dutch liqui point could be ascertained by examining the action of pot them.

(1280) *Allylic Alcohol* (C_6H_5O,HO); *Boiling pt.* 217° iodide of allyl is digested with oxalate of silver, violent act place, double decomposition occurs, in consequence of whic of allyl, and iodide of silver are produced:—

$$\overbrace{2\,C_6H_5I}^{\text{Iodide of allyl.}}+2\,\overbrace{AgO,C_4O_6}^{\text{Oxalate of silver.}}=2\,AgI+2\,\overbrace{C_6H_5O,C_4O_6}^{\text{Oxalate of allyl.}}.$$

The oxalate of allyl or allyl-oxalic ether, is an aromat which boils at 404°: when treated with ammonia it yields and allylic alcohol:—

$$\overbrace{2\,C_6H_5O,C_4O_6}^{\text{Oxalate of allyl.}}+2\,H_3N=2\,\overbrace{(C_6H_5O,HO)}^{\text{Allylic alcohol.}}+\overbrace{(H_2N)_2C_4O_4}^{\text{Oxamide.}}$$

Allylic alcohol is metameric with acetone, and with aldehyd, but it differs from them in properties. It is than water, in which it is soluble in all proportions: its is inflammable, and burns with a luminous flame. When with potassium, hydrogen is evolved, and *potassium-ally* (C_6H_5O,KO) is obtained in the form of a gelatinous mass

Allylic alcohol when mixed with sulphuric acid unites rms *sulphallylic* acid (HO,C_6H_5O,S_2O_6), which corresponds he sulphethylic. It is the vinic acid of the series.

281) *Oxide of Allyl; Allylic Ether* (C_6H_5O,C_6H_5O): *Boils* en 185° and 190°.—When the compound of potassium with alcohol is mixed with iodide of allyl, violent action occurs; of potassium is formed, and allylic ether is produced, by a position analogous to that which attends the formation of ry ether when sodium-alcohol is treated with iodide of ethyl, 5.)

$$\overbrace{\left.\begin{matrix}C_6H_5\\I\end{matrix}\right\}}^{\text{de of allyl.}} + \overbrace{\left.\begin{matrix}C_6H_5\\K\end{matrix}\right\}O_2}^{\text{Potassium-allyl-alcohol.}} = \left.\begin{matrix}K\\I\end{matrix}\right\} + \overbrace{\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}O_2}^{\text{Allylic ether.}}.$$

erthelot and De Luca state that oxide of allyl may also be d by distilling iodide of allyl with red oxide of mercury. It hter than water, and has an ethereal odour resembling that of ks.

xide of allyl appears to exist ready formed in small quantity l of garlic, and in some other oils which resemble it. Wert- also states that it may be obtained by decomposing oil of rd by distillation in a closed tube with hydrate of soda and , but the decomposition of the sulphocyanide of allyl thus ed is slow and imperfect. It enters into direct combination nitrate of silver, and forms a compound (C_6H_5O,AgO,NO_5) may be obtained by mixing rectified essence of garlic with ess of a concentrated alcoholic solution of nitrate of silver: e course of twenty-four hours a black deposit of sulphide of is formed; the liquid must be boiled, and filtered; on cool- the compound of oxide of allyl with nitrate of silver crystal- in brilliant colourless radiated prisms, which are freely soluble ter, but sparingly so in cold alcohol. If this body be dis- d in ammonia, oxide of allyl is set at liberty.

A double allylic ether has also been formed by decomposing e of allyl by an alcoholic solution of potash; in which case *thylic ether* (C_6H_5O,C_4H_5O), a liquid which boils at 144°·5, duced. *Allyl-amylic ether* ($C_6H_5O,C_{10}H_{11}O$) may be obtained stituting a solution of potash in fousel oil for the alcoholic ion of potash used in the previous experiment. It boils

nann and Cahours have obtained the same compounds by ing potassium-allyl-alcohol by iodide of ethyl, and by amyl.

Chloride of Allyl (C_6H_5Cl) is readily obtained by distilling allylic alcohol with chloride of phosphorus, and the *bromide* (C_6H_5Br) may be obtained with equal facility by distilling the alcohol with bromide of phosphorus.

Iodide of Allyl; Iodized Propylene ($C_6H_5I=168$): *Sp. gr. of liquid* 1·789; *Boiling pt.* 214°.—This interesting compound is obtained by the action of equal parts of biniodide of phosphorus and glycerin upon each other (1067). It is a colourless liquid, insoluble in water, but soluble in alcohol and in ether; it has an ethereal, somewhat alliaceous odour; when exposed to air and light it rapidly becomes brown, and emits an irritating odour allied to that of mustard; it may be distilled unaltered. Iodide of allyl is decomposed by digestion with an aqueous solution of ammonia, and on distillation with potash a volatile base of a fishy ammoniacal odour is formed, probably *allylia* ($C_6H_7N=C_6H_5,H_2N$).

The following compounds investigated by Wurtz (*Ann. de Chimie*, III. li. 87) are connected with these bodies:—

(1283) *Bibromide of Tritylene* ($C_6H_6Br_2$): *Boiling pt.* between 284° and 293°.—This is a colourless liquid, having the odour of Dutch liquid. It is most readily prepared by transmitting through bromine the gaseous products procured by passing the vapours of fousel oil through a red-hot tube, and submitting the liquid thus obtained to fractionated distillation. This substance may be regarded as the hydrobromic ether of tritylic glycol.

Bromide of Bromotritylene (C_6H_5Br,Br_2): *Sp. gr. of liquid* 2·392; *Boiling pt.* about 383° F.—When the vapour of the foregoing compound is submitted at its boiling point to the action of the vapour of bromine, the two bodies react upon each other, hydrobromic acid gas is formed, and a new brominated substance having the above formula is obtained. After purification by distillation it is procured in the form of a colourless liquid of a powerfully irritating and very persistent odour. It acts rapidly upon the salts of silver.

A compound, metameric with the foregoing one, which has been termed the *tribromide of allyl*, is obtained by decomposing 1 part of iodide of allyl with 2½ parts of bromine. It boils at 423°, and unlike its isomeride it becomes converted into a solid mass at temperatures below 50°. When cooled slowly it deposits magnificent brilliant prisms fusible at 62°. An alcoholic solution of potash decomposes it, liberating an ethereal compound which boils at 275°.

Tribromide of allyl is readily attacked by acetate of silver, 1 atom of the bromide requiring 3 atoms of the acetate for its decomposition. It is thus converted into triacetin ($C_{18}H_{14}O_{12}$), and this substance, when decomposed by baryta water, yields a pro-at 392°, was

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ulphide
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ay metallic solutions,
num, and palladium,
or of copper. The
lphide of silver being
l and nitrate of silver
tted compound of allyl
nixing alcoholic solutions
blimate, when an abundant
$gS + C_6H_5Cl, 2\,HgCl.)$ If
ocyanide of potassium it is
ed with sulphide of allyl is

$$\overbrace{3(K,C_2NS_2)}^{\text{lphocy. potass.}} = 3\,KCl + 2\,HgS$$

$$\overbrace{H_5S}^{\text{of}\ \text{lic.}} + \overbrace{C_6H_5,C_2NS_2}^{\text{Essence of mustard.}};$$

ide of mercury and allyl is alone
e, chloride of potassium and sulpho-
rmed, whilst the sulphide of allyl
anied by the oil of mustard, leaving
retort.
en the cloves of garlic are distilled with

water, a brown heavy fœtid oil passes over, constituting littl than 0·2 per cent. of the fresh root. It is partially decom by redistillation over an open fire, but if rectified from a ba salt water, about two-thirds of the oil may be obtained in th of a yellowish liquid which is lighter than water, and which, treated with chloride of calcium, and subsequently distilled fragments of potassium, furnishes pure sulphide of allyl. crude oil appears to contain portions of oxide of allyl, and higher sulphuretted compound of allyl, which becomes decom during the distillation.

The *essence of assafœtida* contains a larger proporti sulphur than that of garlic; it evolves sulphuretted hydrogen taneously, and cannot be redistilled without undergoing position.

(1285) *Sulphocyanide of Allyl* (C_6H_5,C_2NS_2): *Sp. gr.* 1·010; *of vapour* 3·54.—This compound constitutes the pr portion of the essential oil of mustard, from which it may tained in a state of purity by simple redistillation; this op frees the essence from a brown resinous matter with wh usually contaminated. The pungency of the horseradish, scurvy grass, and of one or two other allied plants is also the sulphocyanide of allyl. Berthelot and De Luca made teresting observation that when iodide of allyl is distilled sulphocyanide of potassium, an oil is formed identical wi chief constituent of essence of mustard—an observation afforded the first indication of the intimate relation sub between the allylic series and that of glycerin:—

$$\overbrace{C_6H_5I}^{\text{Iodide of allyl.}} + \overbrace{K,C_2NS_2}^{\text{Sulphocy. potass.}} = \overbrace{C_6H_5,C_2NS_2}^{\text{Essence of mustard.}} + KI.$$

The seeds both of the black and of the white must by expression a large quantity of a bland fixed oil, but th not contain any essential oil ready formed; white mustard not yield the sulphocyanide of allyl.* The black mustard,

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* According to Babo and Hirschbrunn, white mustard contains th sulphocyanate of a peculiar alkali, termed *sinapine*, $C_{22}H_{23}NO_{10}$. Th when acted upon by hydrate of potash or soda, is decomposed int acid, and a new alkali, termed *sinkaline*, in the manner represented lowing equation, adopting the altered formula $C_{32}H_{23}NO_{10}$ propose hardt:—

$$\overbrace{C_{32}H_{23}NO_{10}}^{\text{Sinapine.}} + 2\,(KO,HO) = 2\,\overbrace{KO,C_{22}H_{10}O_{8}}^{\text{Sinapate of potash.}} + \overbrace{C_{10}H_{13}NO_{2}}^{\text{Sinkaline.}} + H$$

An aqueous solution of sinapine has an intensely yellow colour. cannot be isolated in a pure condition owing to the facility with wh contains the potash salt of a compound termed *myronic* which is susceptible of a decomposition analogous to that ienced by amygdalin. This decomposition is not effected the crushed seed is moistened with water; a peculiar azotised nt contained in the seed, and analogous to the synaptase of mond, is thus brought into action, and the essential oil is ped.

udwig and Lange (*Knop's Centralblatt,* 1861, p. 149) ob- 1 part of myronate of potash from 500 of black mustard, llized in colourless brilliant needles; and according to their is this salt consists of $KO,C_{20}H_{19}NS_4O_{18}$: it splits into oil stard, sugar, and probably also into bisulphite of potash, lating the elements of water, as follows:—

$$\overbrace{H_{19}NS_4O_{18}}^{\text{ate potash.}}+HO=KO,HO,S_2O_4+\overbrace{C_6H_5,C_2NS_2}^{\text{Oil of mustard.}}+\overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

e essence of mustard is a colourless oil of a burning and lly penetrating odour, which produces a copious flow of tears. essence be applied to the surface of the body, it speedily blister upon the part. Essence of mustard is soluble in portions in alcohol, and in ether, but very sparingly so in if exposed to the air it absorbs oxygen and becomes brown. rified essence boils at 298°; when hot it dissolves both and phosphorus in considerable quantities, but, as the is cool, these bodies are again deposited in crystals. Oil tard can be converted into essence of garlic by heating it e hours in a sealed tube, with sulphide of potassium, at a ature of 250°:—

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ed: it forms crystallizable salts. The hydro-sulphocyanate is ex- rom white mustard, after treating the dried flour successively with l absolute alcohol to remove the fixed oil and colouring matter, and ing the residue in alcohol of sp. gr. 0·825. After the solution has been ly concentrated by evaporation, the salt is deposited in crystals as l cools. If the solution of this salt be mixed with an alkali, it n intensely yellow colour, and on boiling the solution, and subse- dding hydrochloric acid in slight excess, sinapic acid is deposited. water be used to decompose the salt of sinapine, the sinapic acid is ted as an insoluble sinapate of baryta, and sinkaline may be obtained olution. Sinapic acid crystallizes in prisms; it is sparingly soluble ater, very soluble in boiling alcohol, and insoluble in ether; it fuses ture above 300°: nitric acid dissolves it, and produces an intense

may be obtained in deliquescent crystals, which absorb car- m the air; it is a powerful base, but readily undergoes decom- ith bichloride of platinum it forms a magnificent double salt, llizes in orange-coloured six-sided prisms ($C_{10}H_{13}NO_2$,HCl,

$$2\,\overbrace{(C_6H_5,C_2NS_2)}^{\text{Essence of mustard.}}+K_2S_2=\overbrace{(C_6H_5S,C_6H_5S)}^{\text{Essence of garlic.}}+2\,\overbrace{(K,C_2NS_2)}^{\text{Sulphocy. potas.}}$$

(1286) Oil of mustard combines at once with ammoni forms a compound which enters into direct combination wit like a true organic base; from its origin this compound ha termed *thiosinnamine* :—

$$\overbrace{C_6H_5,C_2NS_2}^{\text{Oil of mustard.}}+H_3N=\overbrace{C_8H_8N_2S_2}^{\text{Thiosinnamine.}}\text{ or }\overbrace{H_3(C_6H_5)N_2,C_2S_2}^{\text{Sulphuretted-allyl-urea.}}$$

Thiosinnamine corresponds to the urea of the allyl series, in 2 equivalents of sulphur are present instead of 2 equival oxygen. Sulphocyanide of allyl also unites with other base as ethylia, aniline, and naphthalidine, and forms with the pounds analogous to thiosinnamine.

If thiosinnamine be triturated with red oxide of mercury and sulphide of mercury are formed, and a new basic su free from sulphur, termed *sinnamine,* is obtained :—

$$\overbrace{C_8H_8N_2S_2}^{\text{Thiosinnamine.}}+Hg_2O_2=Hg_2S_2+H_2O_2+\overbrace{C_8H_6N_2}^{\text{Sinnamine.}}$$

Oxide of lead produces a similar decomposition.

Sinnamine has been regarded as a compound amm which one equivalent of hydrogen has been displaced by al a second equivalent by cyanogen, thus :—

$$C_8H_6N_2=\left.\begin{matrix}H\\C_6H_5\\C_2N\end{matrix}\right\}N;\text{ or }\textit{cyanallylia.}$$

Sinnamine is soluble in water, and may be obtained in pr crystals. It is a powerful base, and expels ammonia f salts. It occasions precipitates in solutions of lead, of ir of copper. The oxalate is the only salt of sinnamine whic tallizes readily; solutions of the salts of sinnamine which an excess of acid impart a yellow colour to a slip of deal.

(1287) *Sinapoline* ($C_{14}H_{12}N_2O_2=140$).—This base is formed by digesting essence of mustard upon hydrated lead :—

$$2\,C_8H_5NS_2+6\,(PbO,HO)=C_{14}H_{12}N_2O_2+4\,PbS+2\,PbO,C_2O_4+2$$

but it may also be produced by the action of water up cyanic ether, which will be immediately described. Sinap a feeble base which crystallizes from its solution in brilliant greasy flakes: it fuses below 212°. Its aqueous occasions a precipitate in solutions of corrosive sublimate bichloride of platinum.

8) Hofmann and Cahours have also obtained a variety of d allylic ethers. These bodies have an ethereal odour ecals that of mustard. The most interesting of them are ate and the cyanate. *Allyl-cyanic ether* or *cyanate of* $_6H_5O,C_2NO$; *Sp. gr. of vapour* 3·045), is prepared by pon cyanate of silver with iodide of allyl; the heat gene- the reaction is sufficient to cause the distillation of the hilst iodide of silver remains in the retort. A colourless thus obtained which boils at 180°; its vapour possesses nsely penetrating odour, and produces a copious flow of When this ether is gently warmed with a solution of am- it is dissolved, and the solution on evaporation deposits cent crystals of allylic urea:—

$$\overbrace{C_6H_5O,C_2NO}^{\text{Allyl-cyanic ether.}}+H_3N=\overbrace{H_3(C_6H_5)N_2,C_2O_2}^{\text{Allyl-urea.}}.$$

ponding crystalline compounds may be obtained if methylia, , amylia, or aniline be substituted for ammonia. When yanic ether is treated with water, carbonic acid is elimi- and the ether is slowly converted into *sinapoline* $_2N_2O_2$), which by its production in this manner is shown to *llyl-urea* :—

$$\overbrace{2\,(C_6H_5O,C_2NO)}^{\text{Allyl-cyanic ether.}}+H_2O_2=\overbrace{H_2(C_6H_5)_2N_2,C_2O_2}^{\text{Sinapoline.}}+C_2O_4.$$

89) *Allylia.*—A concentrated solution of potash decomposes yanic ether; sinapoline is formed, and if the liquid be dis- *allylia,* a basic substance which boils between 356° and 374°, over, mixed with methylia and tritylia. Allylia is the alkali of the allylic series, which corresponds to ethylia in ylic series:—

$$\overbrace{C_6H_5O,C_2NO}^{\text{Allyl-cyanic ether.}}+2\,(KO,HO)=\overbrace{C_6H_5,H_2N}^{\text{Allylia.}}+2\,KO,C_2O_4.$$

e following table gives a synoptic view of the principal nds in the allylic series:—

. . . .	C_6H_5,C_6H_5	Sulphallylic acid	HO,C_6H_5O,S_2O_6
lcohol .	C_6H_5O,HO	Allyl-oxalic ether	$2\,C_6H_5O,C_4O_6$
ther . .	C_6H_5O,C_6H_5O		
ylic	C_6H_5O,C_4H_5O	Allyl-oxamic ether	C_6H_5O,H_2N,C_4O
of allyl	C_6H_5S,C_6H_5S	Allyl-carbonic ether	$2\,C_6H_5O,C_2O$
of do. .	C_6H_5Cl		
of do. .	C_6H_5Br	Allyl-acetic ether	$C_6H_5O,C_4H_3O_3$
f do. .	C_6H_5I		
yanide	C_6H_5,C_2NS_2	Allyl-benzoic ether	$C_6H_5O,C_{14}H_5O_3$

Allyl-cyanic ether	C_6H_5O,C_2NO	Sulphallyl-urea (thiosinnamine)	$H_2(C_6H_5)$
Allylia . . .	C_6H_5,H_2N	Acrolein (acrylic aldehyd)	$C_6H_3O_2$
Cyanallylia (sinnamine)	$(C_6H_5,C_2N,H)N$	Acrylic acid . .	HO,C_6H_3
Allyl-urea . .	$H_3(C_6H_5)N_2,C_2O_2$		
Diallyl-urea (sinapoline)	$H_2(C_6H_5)_2N_2,C_2O_2$		

§ II. Resins.

(1290) These substances are produced by certain fam
plants in considerable abundance, and they also are very nu
They have a considerable commercial value, and are ext
employed in the preparation of the different kinds of
They are generally obtained by making incisions into the
trees which produce them, when they exude in the form of
liquid, consisting of the resin in solution in the esse
of the plant. In the majority of cases they are formed
oxidation of the essential oils contained in the trees;
is not surprising that in many instances they have the
sition of oxides of the hydrocarbon $C_{40}H_{32}$, or of a hyd
derived from this, having lost a certain number of equiv
hydrogen in exchange for an equal number of atoms of ox

As a class, the resins are insoluble in water, but they ar
in alcohol, especially when heated with it; many of them
obtained from this solution in crystals by evaporation.
siderable number of them possess acid characters, in wh
their alcoholic solutions redden litmus. The acid resins
with the alkalies, and remain soluble in alkaline leys; th
tions, when agitated, produce a lather like that furni
soap, but they are not precipitated like ordinary soap on t
tion of chloride of sodium. Like the essential oils, the
resins are usually mixtures of two or more resins, which oft
of separation by their unequal solubility in different mens

The resins are transparent or translucent brittle soli
are insulators of electricity, and become negatively electric
tion; they fuse at a moderate temperature, are very infla
and burn with a white smoky flame. If heated in close
they undergo decomposition, and yield various forms of hydr

Common rosin is thus found to furnish the following
among others which have been less perfectly investigated

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* Mr. Hunt has recently contrived a method of distilling comm
a current of superheated steam, by which means he has been enable
rate and purify these different resinous acids on a very large s
manufacture of soap.

Hydrocarbons.	Formulæ.	Boiling point ° F.	Specific gravity.	
			Liquid.	Vapour.
erebene	$C_{20}H_{16}$	320°	0·86	4·81
olophene	$C_{40}H_{32}$	599°	0·94	
esinein	$C_{40}H_{28}O_2$	482°		
etinaphtha or Toluol	$C_{14}H_8$	226°	0·86	3·23
etinyl or Cumol . .	$C_{18}H_{12}$	302°	0·87	4·24
etinol	$C_{32}H_{16}$	460°	0·90	7·11
aphthalin	$C_{20}H_8$	428°		4·528
etanaphthalin . .	$C_{40}H_{16}$?	617°		

1291) *Common Rosin* or *Colophony.*—When ordinary tur-
ue is distilled with water, it leaves a residue of rosin amount-
o from 75 to 90 per cent. of the turpentine employed. There
wo principal kinds of rosin in the market, a brown and a white

. The brown variety is furnished by the *Pinus abies;* it is an
r-coloured brittle solid, which consists of two distinct but
eric resinous acids, the *sylvic* and *pinic* ($HO,C_{40}H_{29}O_3$;
ent). Cold alcohol (sp. gr. 0·87) dissolves the pinic acid, which
s the larger proportion of the resin, and leaves it on evapora-
is an amorphous mass. It may be purified from adhering
of a neutral resin by precipitating its solution in cold alcohol
he addition of an alcoholic solution of acetate of copper. The
te of copper thus precipitated may then be decomposed by
acid. When pinic acid is heated to partial decomposition, the
ue in the retort is found to consist of another isomeric resinous
, the *colopholic;* it neutralizes bases more perfectly than pinic
, and is much less soluble in alcohol (Unverdorben).

The other constituent of rosin, *sylvic* acid, may be obtained
its solution in hot alcohol, in colourless rhombic prisms or
es, fusible at 260°. Its ethereal solution expels carbonic acid
the alkaline carbonates. It forms with oxide of lead a salt
h crystallizes in slender four-sided needles.

White resin or *galipot* is obtained from Bordeaux turpentine,
ished by the *Pinus maritima,* and consists almost entirely of
al resin, the *pimaric,* which is isomeric with the preceding.
acid may be extracted by removing from the powdered resin
bstances which are soluble in a mixture of six parts of cold
ol and one of ether: the residue, if treated with boiling
ol, deposits pimaric acid as it cools. When the alcoholic
ion of pimaric acid is evaporated, the acid is deposited in
es indistinctly crystallized. If this acid be melted and allowed
ol, it yields a colourless glass as clear as crystal: this melted
when powdered is dissolved by an equal weight of alcohol, but

the solution thus obtained, if left for a few-minutes, suddenl to deposit elliptical crystals, which require for solution t their weight of alcohol, and possess all the properties of acid before fusion. Pimaric acid is freely soluble in et it be distilled in vessels from which air is excluded, the is found to consist principally of another isomeric resin *pyromaric acid*, distinguished by forming with lead a sa crystallizes in delicate needles. Pyromaric acid, acco Gerhardt, is identical with sylvic acid.

Ordinary rosin is dissolved completely by alkaline enters largely into the formation of yellow soap.

If nitric acid be boiled upon ordinary rosin, the com oxidized and dissolved, and on evaporating the solution to sistence of a syrup, it deposits when left to itself for som small four-sided prisms with an oblique terminal face. stance is named *terebic acid* ($HO,C_{14}H_9O_7$). It is soluble in cold water, but much more soluble in boiling well as in alcohol and ether; it requires a high temperatu fusion, and is decomposed at about 400°.

(1292) *Varnishes.*—The resins most extensively em the preparation of the different kinds of varnish are copal (from the *Hymenæa verrucosa ?*), mastich (from t *chia lentiscus*), sandarach (from the *Juniperus commu* and occasionally those of elemi and anime. Copal is a har colourless, transparent resin, which is dissolved with dif the state in which it is imported; but if powdered and e the air for some weeks, or if fused so as to enable it oxygen, it is more readily attacked by solvents.

The solvents employed in preparing varnishes are o pentine, wood naphtha and spirit of wine; the resin bef added to the solvent must be pulverized, and afterwar with broken glass in order to prevent the powder from a ting into lumps. When the varnish is spread over the s any object which it is intended to protect, the solvent e and leaves a thin transparent coating of resin. The spirit nishes dry the most rapidly, but they are apt to crack off. This defect is partially remedied in the turpentine which dry more slowly; and it is still more effectually o what are termed oil varnishes, in which a small quantity drying oil, such as that of linseed or of poppy, is add solution in rectified turpentine: these varnishes requir siderable time for complete hardening, but they are very The common varnish used for oil paintings and maps c arts of mastic, 3 of Venice turpentine, and 1 of camphor; e are mixed with 10 parts of pounded glass, and dissolved in f rectified oil of turpentine.

(1293) GUAIACUM resin is the exudation of the *Guaiacum* *inale.* It is of a dark greenish-brown colour, and is readily erized. It has a taste which is at first slight, but afterwards mes acrid and hot; its odour is feeble, but resembles that of in. Alcohol dissolves the greater part of this resin; ether s not dissolve it so completely, and it is insoluble in the fixed oils. is also freely soluble in a solution of potash and in oil of vitriol. alcoholic tincture yields a blue precipitate when acted on by orine: with sulphuric acid it gives a green precipitate. White r when stained with tincture of guaiacum acquires a pale low tint; and if this be exposed to the more refrangible rays the solar spectrum, it becomes of a fine blue or greenish-blue ur. The pale yellow tint is restored when the altered paper xposed in the less refrangible portion of the spectrum, or when ntle heat is applied to it. This restoration of the colour de- ds upon the absorption of oxygen: powdered guaiacum when sed to the air absorbs oxygen and becomes green. Fuming c acid dissolves the resin and acquires a green colour; if a ain quantity of water be added, a green precipitate is formed, the solution becomes blue, but the addition of a larger quan- of water renders the precipitate blue and the solution brown.

Resin of guaiacum appears to consist of two distinct resinous s, one of which, *guaiacic acid* ($HO,C_{12}H_7O_5$; Deville), may be ined from its alcoholic solution, crystallized in beautiful needles, h are freely soluble in water.

Guaiacum resin melts at a moderate heat, and begins to undergo mposition at about 600°. Amongst the products of its de- ctive distillation Deville enumerates three definite com- nds:—1. A light volatile oil, *guaiacene* ($C_{10}H_8O_2$), of sp. gr. 4: it boils at 244°, giving off a vapour of sp. gr. 2·92, and it rbs oxygen from the air, forming a beautiful crystalline com- nd. 2.—A volatile compound, *pyroguaiacin* ($C_{38}H_{22}O_6$), which llizes in pearly scales. And, 3—An oil heavier than water, d *hydride of guaiacyl* ($C_{14}H_8O_4$); this liquid boils at about °, emitting a vapour of sp. gr. 4·49. It is soluble in alcohol, , and acetic acid, but not in water.

(1294) LAC.—One of the most valuable of the resins is lac, h occurs in commerce under three distinct forms; viz., as *-lac*, *seed-lac*, and *shell-lac.* This resin exudes from the branches of several trees in tropical climates, and in particular from the *Ficus indica*, *Ficus religiosa*, and *Rhamnus jujuba*, in consequence of the punctures of the female of a small insect of the cochineal tribe, the *Coccus ficus;* the resinous juice which exudes hardens over the insects. The young shoots when cut off, covered with the resin, and enclosing the cocci, constitute stick-lac. The crude stick-lac is then bruised, and the fragments of the branches are removed; after which the resinous mass is digested in a weak solution of carbonate of soda, by which means a red colouring matter contained in the insects is extracted. This material is now extensively used as a dye, and has largely displaced the more expensive cochineal. The residue which is insoluble in the alkaline ley, forms the commercial *seed-lac*. When this is melted, strained through a long cotton bag, and the viscous resin while soft compressed into flat sheets, between leaves or stones, it forms the scaly purified mass which is sold under the name of *shell-lac*. This resin appears to consist of a mixture of four or five distinct compounds, one of which is acid and may be obtained in crystals, and according to Unverdorben, it also contains both oleic and margaric (palmitic) acids. It is soluble in an aqueous solution of borax, by which it may be distinguished from most common resins with which it is sometimes adulterated.

Lac is extensively used as a stiffening for hats, and it forms the principal constituent of the better kinds of sealing-wax. Red sealing-wax owes its brilliant colour to vermilion; 48 parts of shell-lac, 12 of Venetian turpentine, 1 part of balsam of Peru, melted at a gentle heat, and incorporated with 36 parts of vermilion, furnishes red sealing-wax of the best quality (Löwig). When lac is mixed with half its weight of sandarach, and a small quantity of Venice turpentine, it forms with 10 or 12 parts of alcohol a varnish, technically termed *lacquer*, which is much employed for heightening the colour of brass and bronzed articles.

(1295) BALSAMS.—The soft viscous resins which consist of a large mixture of essential oil with the resin, are termed balsams; such, for example, as balsam of copaiba, and balsam of Canada. Some of them contain in addition benzoic or cinnamic acid, as in the case of the balsams of benzoin, tolu, storax, and Peru.

Balsam of Copaiba is obtained from several species of *Copaifera*. It consists of a volatile essential oil isomeric with oil of turpentine; a resinous acid, *capivic acid* $C_{40}H_{30}O_4$, isomeric with pinic acid; and a viscous neutral resin. *Balsam of Canada* is the nearly colourless liquid resin of the *Pinus balsamea*.

(1296) GUM RESINS are the milky juices of many plants, solidified by exposure to air. They consist chiefly of the peculiar resins and essential oils of the plants, mixed with a large proportion of gum; consequently they produce when rubbed up with water, a milky-looking liquid, or emulsion, the gum becoming dissolved, and retaining the resin and oil in suspension. Dilute alcohol dissolves the gum resins in great measure, as do also weak alkaline solutions. The gum resins form a numerous and important class of medicinal remedies. Ammoniacum, assafœtida, aloes, euphorbium, galbanum, gamboge, myrrh, olibanum, and scammony, all belong to this class of bodies.

(1297) Amber.—Some fossil substances approach more closely to the resins than to any other class of compounds; of these, one of the most important is *amber*. It is a light-yellow, transparent substance, with a density generally a little greater than that of water. Its property of becoming electric by friction is familiarly known. It occurs often in beds of wood coal, but is chiefly found after storms, on the coasts of the Baltic, between Königsberg and Memel. Amber consists of a mixture of several resinous bodies, which have not been accurately examined; about one-eighth of its weight is soluble in alcohol, and about one-tenth of it is soluble in ether. If heated in closed vessels it melts, gives off succinic acid, water, and a peculiar empyreumatic oil, which consists of a mixture of several hydrocarbons having nearly the same composition as oil of turpentine. The succinic acid appears to be furnished solely by that portion of the resin which is soluble in ether (Schrötter). A small quantity of succinic acid exists ready formed in the resin, and can be extracted by digesting powdered amber in an alkaline solution. The empyreumatic oil is furnished principally by the bituminous portion, which is insoluble in ether and in alcohol. Amber, when treated with nitric acid, is gradually dissolved; succinic acid crystallizes from the solution when concentrated, and ordinary camphor is found in the distillate.

(1298) Caoutchouc or *Indian-rubber* (xC_5H_4): *Sp. gr.* from 0·92 to 0·96.—This substance occurs in small quantities in the juices of many plants, particularly of the *Urticaceæ*, *Euphorbiaceæ*, and *Apocynaceæ*. Its available supply, however, is the spontaneously solidified milky juice of the *Hævæa elastica*, *Jatropha elastica*, and some other tropical plants. As first procured by incisions into the stem of the plant, it appears as a yellowish milky fluid which, in addition to caoutchouc, contains albumen; the albumen occasions the juice on being boiled to coagulate. When the fresh juice is exposed to the air in thin films, it speedily dries, and hardens into elastic layers of brownish yellow caout-

chouc. The caoutchouc is not dissolved in the
suspended in it, and when the liquid is dilute
to the surface like cream; when once become
again be diffused through water. Commerci
the mode of its preparation, retains the albu
stituents of the juice, but pure caoutchouc is
hydrocarbon (Faraday). In its solid conditi
elastic, especially when warm. Although ins
softens considerably in this liquid at the boilir
is thereby rendered more easily acted upon by i
Caoutchouc may be preserved unaltered for an i
cluded from the light, but if exposed in the air
diffused daylight it gradually absorbs oxygen an
into a viscid mass which has lost its elasticit
alcohol. Alkaline solutions are without effec
Even chlorine attacks it very slowly; concentr
phuric acids decompose it, but when dilute the

The proper solvents of caoutchouc are w
form, bisulphide of carbon, coal naphtha, and re
tine. In these liquids it first swells up ver
eventually forms a ropy liquid, which on evapo
caoutchouc with its original elasticity. This p
account in the manufacture of various waterp
articles. According to Payen, caoutchouc con
one of which is soluble in the liquids above m
other portion merely softens and swells up, bu
true solution. Caoutchouc is also dissolved b
its elasticity is thereby destroyed. Waterproo
by varnishing one surface of a fabric construc
with a solution of caoutchouc, then bringing i
a second sheet similarly prepared, and passin
between rollers. The freshly cut edges or su
caoutchouc cohere readily; this property, wi
elasticity, together with its power of resist
agents, renders it invaluable in the laboratory
tubes and joints, used in connecting apparatus
tight manner. Caoutchouc melts at a heat of
after it has been melted it does not solidify on
a sticky mass which does not become solid ev
the air for months. Owing to this property it
material for the lubrication of stop-cocks, and
remain moveable yet air-tight. If caoutchouc
in the open air it takes fire, and burns with a br

f distilled in closed vessels, caoutchouc furnishes a mix- of several different hydrocarbons of the general formula H_8).

o the most volatile of these Williams has given the name prene ($C_{10}H_8$): *Sp. gr. of liquid* 0·6823; *of vapour* 2·43; *g pt.* 99°.—It remains liquid at very low temperatures. ydrocarbon slowly absorbs oxygen when exposed to the air, ing viscid, and acquiring the power of bleaching a solution of te of indigo. If in this state it be submitted to careful distil- unchanged isoprene passes over, and at a particular stage, the ts of the retort suddenly thicken, and become converted into white spongy elastic mass, consisting of $C_8H_{10}O$.

another of these hydrocarbons which has exactly double the of isoprene, Himly has given the name of *caoutchine* $_{16}$: *Sp. gr. of liquid* 0·842; *of vapour* 4·65; *Boiling pt.* it is isomeric with oil of turpentine, which it resembles in miscible in all proportions with alcohol, ether, and the fixed latile oils. It may be exposed to a cold of −22° without ing solid; it dissolves caoutchouc freely. Greville Williams, ing on this compound with bromine, has obtained the body Br_2; and on treating this with an amalgam of sodium, has ted it into cumol, $C_{20}H_{14}$.

chardat found, among the less volatile portions of the oil, a oily hydrocarbon, *heveène*, which he considered to be poly- with olefiant gas, though this is doubtful. It had a sp. gr. 1, and boiled at 599°.

99) A highly valuable modification of caoutchouc, dis- d by Goodyear, has lately been introduced into the arts under e of *vulcanized* Indian rubber, which from its almost per- sticity at all temperatures below that of 240°, admits of a of useful applications. The cut edges of this form of ouc do not cohere by pressure, and it does not become e to other bodies at temperatures below 212°. Caoutchouc immersed in the form of sheet in melted sulphur at 250° lly imbibes from 12 to 15 per cent. of its weight of sulphur, does not at this temperature experience any change in its l or chemical properties. If, however, such sulphurized be heated for a few minutes to about 300°, the peculiar dification is produced, and if the temperature be allowed uch higher than this, the mass becomes black, hard , and is changed into a substance which has been intro- the arts under the name of *vulcanite*, or *ebonite*, and nany of the purposes for which horn is fitted. At a

Eastern archipelago.
ays to the tree which
r six feet, and though
n oil fit for food. On
he wood, a milky juice
a percha is a tough in-
peratures retains any shape
, but below 212° it becomes
x, and indeed may be em-
, since it will copy the finest
, and a variety of useful and
ith great facility. It also
lding together when in this
aces are quite free from any
n becomes hard, and is pos-
It is, when pure, of a pale
odour somewhat resembling
becomes negatively electric,
city; and this property has
e covering of wires for tele-
o largely used as a water-
as a substitute for leather
rnishes a valuable material
eying liquids; it is likewise
the construction of bands
receiving new and useful

n water, it is not attacked
but it is dissolved readily by
on, oil of turpentine, and the
l moderately it melts; and
lding hydrocarbons identical
). Solutions of the alkalies
a. Hydrochloric and dilute
atė acids in general, have no
in the preparation of bottles
se liquids. The principal
y of preventing it from re-
which allows the slow trans-
Concentrated nitric acid
nd oil of vitriol produces the

a *consists* of three distinct

temperature a few degrees beyond that necessary to the production of vulcanite the mass is converted into a hard brittle substance, which at a higher temperature undergoes carbonization and decomposition. Ebonite, or vulcanite, is one of the best insulators of electricity that is known, and becomes powerfully negatively electric when excited by friction. Vulcanized caoutchouc appears to consist of a combination of the elastic gum with 2 or 3 per cent. of its weight of sulphur. The excess of sulphur which is usually present is only mechanically distributed through the mass, and may be removed by the use of solvents, such as benzol or sulphite of soda. This excess of sulphur is injurious to the elasticity of the material, and gradually renders it brittle and rotten. Several modes of effecting the combination of sulphur with caoutchouc are employed. One of the most useful consists in dissolving the caoutchouc in turpentine in which the proper proportion of sulphur had been previously dissolved: on allowing the solvent to evaporate, the mixture of caoutchouc and sulphur is left endued with the properties of common caoutchouc, and may be easily moulded into the form of the various articles required: it is only on the application of a temperature ranging from 270° to 300° that the peculiar properties of the sulphurized compound are developed. The heat is most advantageously applied by exposing the articles to the direct action of high pressure steam at 270° or 280°. A still easier method adapted for thin articles consists in immersing the caoutchouc for a few moments in a solution of 1 part of chloride of sulphur in 60 of bisulphide of carbon: by simple exposure of the object thus treated to the air, it assumes the character of vulcanized caoutchouc without the aid of heat. The addition of a certain proportion of carbonate of lead to the compound is found to produce an article better adapted for some purposes, such as the manufacture of overshoes or goloshes, than one in which sulphur only is used; due proportions of sulphur and of the salt of lead are incorporated with the caoutchouc by causing the caoutchouc mixed with the other ingredients to pass repeatedly between polished hollow iron rollers maintained at a temperature of about 170°, by the injection of steam into their interior. Vulcanized Indian-rubber withstands prolonged digestion in naphtha or turpentine without undergoing solution.

(1300) GUTTA PERCHA.—This substance, which is similar in chemical properties to caoutchouc, was introduced into this country as an article of commerce about the year 1844. Gutta percha is the concrete juice of the *Isonandra percha*, a tree belonging to the family of the *Sapotaceæ*, which grows abundantly in gapore, Borneo, and other islands of the Eastern archipelago. name *percha* is that given by the Malays to the tree which uces it; it grows to a diameter of five or six feet, and though mber it is valueless, the fruit yields an oil fit for food. On ing notches through the bark into the wood, a milky juice es, which speedily solidifies. Gutta percha is a tough in- ic substance, which at ordinary temperatures retains any shape h may have been impressed upon it, but below 212° it becomes ft that it may be moulded like wax, and indeed may be em- ed for taking casts and impressions, since it will copy the finest with fidelity; beautiful mouldings, and a variety of useful and nental articles are thus made with great facility. It also sses the valuable property of welding together when in this condition, provided that the surfaces are quite free from any of moisture. Below 110° it again becomes hard, and is pos- d of extraordinary tenacity. It is, when pure, of a pale n colour, possessing a peculiar odour somewhat resembling of caoutchouc. When rubbed it becomes negatively electric, f dry it is an insulator of electricity; and this property has o its extensive employment in the covering of wires for tele- ic purposes (260). It is also largely used as a water- ing material, and is employed as a substitute for leather oling boots and shoes. It furnishes a valuable material e preparation of tubes for conveying liquids; it is likewise as a substitute for leather in the construction of bands driving machinery, and is daily receiving new and useful cations.

utta percha is quite insoluble in water, it is not attacked ckholm tar, or by linseed oil; but it is dissolved readily by , chloroform, bisulphide of carbon, oil of turpentine, and the al oils in general. If heated moderately it melts; and this point is decomposed, yielding hydrocarbons identical ose from caoutchouc (Williams). Solutions of the alkalies hout action upon gutta percha. Hydrochloric and dilute uoric acids, as well as the dilute acids in general, have no upon it; hence it is employed in the preparation of bottles essels used for containing these liquids. The principal ack to this use is the difficulty of preventing it from re- certain degree of porosity, which allows the slow trans- of liquids through its mass. Concentrated nitric acid nd disintegrates it rapidly, and oil of vitriol produces the t more gradually.

d commercial gutta percha consists of three distinct

portions, the most abundant of these, the *pure gutta*,
from 75 to 82 per cent. of the mass; it is milk-white
at about 300°; it is insoluble in alcohol, but it is solubl
This substance is a hydrocarbon of the form $C_{40}H_{32}$
two constituents are a white and a yellow resin, both of
soluble in boiling alcohol; but the white resin $(C_{40}H_{32}O$
insoluble in this liquid when cold; by deposition fr
alcoholic solution it may be obtained crystallized
plates, disposed in radiated tufts. The yellow resin (C
amorphous. Pure gutta percha, indeed, slowly absor
when exposed to the combined influence of light and
air, and is gradually converted into a brittle resin freely
hot alcohol. It then entirely loses its plastic charact
may be preserved in the dark or under water for an
period without change.

(1301) RESIN OF JALAP.—This substance has been
subject of numerous careful experiments. It may b
in a colourless form by treating the chopped roots of
boiling water, repeatedly submitting them to pressur
each operation, and when the expressed liquid is
coloured, extracting the resin from the undissolved
means of boiling alcohol (sp. gr. 0·880). This resin a
from 10 to 15 per cent. of the weight of the root operat
is a mixture of two definite resins. One of these (*parar*
is soluble in ether, and is powerfully acid; it has th
odour and acrid taste of jalap. It does not crystalli
alcoholic or ethereal solutions, but if these be mixed with
semi-solid mass which is formed becomes gradually
needle-shaped crystals; it may be sublimed. Accordi
analysis of Johnston it may be represented as $(C_{40}H_{34}O$

The resin which is insoluble in ether (*jalapin* or *rh*
is remarkable for being susceptible of decomposition in
and a resinous acid. Jalapin, according to Spirgatis,
with the active principle of scammony. Jalapin is
destitute of odour and taste. It is fusible at 300°. Al
acetic acid dissolve it readily. It is also easily soluble i
solutions, especially if boiled with them. Mayer ter
volvulin, and assigns to it the formula $(C_{62}H_{50}O_{32})$.
appears to constitute the purgative principle of the jala
vitriol dissolves it slowly, and assumes a beautiful red col
gradually passes into brown. On dilution an oily-lo
body $(HO,O_{32}H_{29}O_5)$ is precipitated, and glucose remai
tion. According to Mayer, the fusiform variety of jala

volus orizabensis) contains a resin homologous with rhodeoretin ($C_{68}H_{56}O_{32}$), which when treated with sulphuric acid is similarly decomposed, glucose remaining in the solution.

§ III. GLUCOSIDES, OR COMPOUNDS WHICH FURNISH GLUCOSE.

(1302) In the course of the present chapter some crystalline compounds have been described which, like amygdalin, salicin, and populin, under certain circumstances break up into glucose, and into some compound or compounds characteristic of the substance from which it is derived. The simplest condition under which this transformation is effected consists in exposing the compound to the action of water at a high temperature under pressure; salicin and phloridzin may thus be made to furnish glucose. The compounds which yield sugar when broken up by any of these processes are termed *glucosides*. They may be subdivided into two classes: one of these consists of neutral substances, like amygdalin and salicin; the other consists of acid bodies, such as gallotannic acid. We shall now proceed to notice some of these compounds; viz., phloridzin, quercitrin, datiscin, arbutin, esculin, and saponin, with one or two others.

(1303) PHLORIDZIN ($C_{42}H_{24}O_{20}+4$ Aq; Strecker).—This is a substance which occurs in the bark of the apple, pear, cherry, and plum, and probably in that of other fruit trees. In order to extract it, it is sufficient to boil the bark for some time with water, and to allow the liquid to cool. Phloridzin is deposited in silky crystals, which may be purified by redissolving them in water, digesting with animal charcoal, and recrystallizing. It has a slightly bitter flavour, followed by a sweetish taste. It requires upwards of 1000 parts of cold water for solution, but it is largely soluble in boiling water. Alcohol and wood spirit dissolve it freely, but it is nearly insoluble in ether. Its alcoholic solution causes left-handed rotation in a ray of polarized light. When heated to 212° it loses four equivalents of water, and at a temperature between 223° and 228° it undergoes fusion, after which, by an additional elevation of temperature, without undergoing any further loss of water, it becomes solid, and does not melt again until the temperature has been raised to 320°. At 392° it again begins to give off water, and assume a red colour, forming a resinoid body ($C_{42}H_{20}O_{16}$), termed *rufin;* this substance is soluble in alcohol: boiling water also dissolves it, but the solution is entirely colourless.

An aqueous solution of phloridzin yields a white precipi

with one of subacetate of lead (6 $PbO,C_{42}H_{24}O_{20}$?). It al
compounds with baryta and lime, but these substances
brown by exposure to air.

Phloridzin, when boiled with weak acids, is decompo
grape sugar, and a resinous matter termed *phloretin*:—

$$\overbrace{C_{42}H_{24}O_{20}}^{\text{Phloridzin.}}+2\,H_2O_2=\overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}+\overbrace{C_{30}H_{14}O_{10}}^{\text{Phloretin.}}.$$

Phloridzin, under the combined influence of air and
yields a red, bitter, uncrystallizable compound termed p
($C_{42}H_{30}N_2O_{26}$), which is readily soluble in boiling water.
phloridzin is exposed to the vapour of ammonia, it p
beautiful blue compound with a coppery lustre, which app
a compound of phlorizein with ammonia; this substance
soluble in water, and cannot be obtained in crystals; sul
hydrogen and other deoxidizing agents destroy this blu
but it is restored by exposure to the air.

Phloridzin does not yield any essential oil when tre
chromic acid or other oxidizing agents; in this respect it
an important difference from salicin, which in other points
resembles.

(1304) QUERCITRIN ($C_{36}H_{18}O_{20}+2\,Aq$).—This sub
homologous with phloridzin, and contains 3 (C_2H_2) less
body. Quercitrin is the yellow, crystallizable colouring ma
tained in the bark of the quercitron or *Quercus tinctoria.*
be extracted from the bark by means of alcohol, sp. gr. c
tannic acid is removed by the addition of gelatin, and t
on evaporation yields quercitrin, which may be purified b
tallization from alcohol. It is sparingly soluble in boili
and in ether, but is readily dissolved by hot acetic acid, a
by weak solutions of the alkalies, with which it forms a li
greenish-yellow colour, which gradually passes into dark-br
solution of alum slowly develops a beautiful yellow colo
solutions. Solutions of acetate of lead, acetate of cop
chloride of tin, precipitate it in yellow flocculi. With pe
of iron it produces an olive-green colour. When quer
boiled with dilute sulphuric or hydrochloric acid, it is dec
into glucose and *quercetin* ($C_{24}H_8O_{10}$), a substance sparingl
in water, but readily soluble in alcohol: it may be obta
minute lemon-yellow crystals. Quercetin is also soluble
tions of potash and of soda, to which it communicates a
yellow colour. The decomposition of quercitrin by acids
thus represented:—

$$\overbrace{C_{36}H_{18}O_{20}}^{\text{Quercitrin.}}+2\,H_2O_2=\overbrace{C_{24}H_8O_{10}}^{\text{Quercetin.}}+\overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

(1305) DATISCIN ($C_{42}H_{22}O_{24}$) is the name given to a crys-ine colourless substance extracted from the *Datisca cannabina*, leaves of which furnish a yellow colouring matter extensively d in India for dyeing silk. It is largely soluble in alcohol and boiling water, sparingly so in cold water and in ether. It gives low lakes with oxides of lead and tin, and forms intensely yellow utions with the alkalies. Dilute acids, when boiled with iscin, cause it to split into glucose and *datiscetin* ($C_{30}H_{10}O_{12}$), a stance which crystallizes in colourless needles, soluble in ether d in alcohol, but nearly insoluble in water. (Stenhouse.)

(1306) ARBUTIN ($C_{24}H_{16}O_{14}=272$; Strecker) is a crystallizable ciple contained in the leaves of the *Arctostaphylos uva ursi*, ich when treated with synaptase is decomposed into glucose, and rystalline body originally termed *arctuvin*, but which Strecker s to be identical with hydroquinone. Arbutin according this chemist is not a homologue of salicin, though it differs n it in containing C_2H_2 less; the following equation re-senting the decomposition of arbutin under the influence of aptase:—

$$\overbrace{C_{24}H_{16}O_{14}}^{\text{Arbutin.}}+2\,H_2O_2=\overbrace{C_{12}H_6O_4}^{\text{Hydroquinone.}}+\overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}.$$

(1307) ESCULIN or *polychrome* ($C_{42}H_{24}O_{26}$; at 212°).—This stance is contained in the bark of the horse-chestnut. In r to extract it, the aqueous infusion of the bark is treated with ate of lead, and filtered, the excess of lead is removed by s of sulphuretted hydrogen, and the liquid is evaporated to consistence of a syrup; in the course of a few days the esculin tallizes: it may be washed with cold water, and recrystallized from weak alcohol (sp. gr. 0·940), and afterwards from boiling er. Esculin forms small colourless needles, which have a bitter e and a slightly acid reaction. It is sparingly soluble in cold er and in ether, but is dissolved abundantly by boiling water, less freely by hot alcohol. Solutions of esculin are particularly arkable for their fluorescent power, in consequence of which appear in certain positions to be deep blue, although colourless d by transmitted light. Acids destroy this property, but the n of an alkali to the liquid heightens the fluorescent er. Esculin fuses and loses water when heated to 320°; gher temperature it is decomposed, emitting an odour of sugar, whilst a small quantity of esculetin is sublimed in

Esculin when boiled with dilute acids, or when digeste synaptase, undergoes decomposition into esculetin and gluco

$$\overbrace{C_{42}H_{24}O_{26}}^{\text{Esculin.}}+5\,H_2O_2=\overbrace{C_{18}H_6O_8}^{\text{Esculetin.}}+2\,\overbrace{C_{12}H_{14}O_{14}}^{\text{Glucose.}}$$

Esculetin is a substance which has a slightly acid reactio litmus; it is sparingly soluble in cold water, in cold alcoho in ether; but it is freely soluble in boiling alcohol, which d it in crystalline needles or plates resembling those of benzoi Esculetin is soluble in solutions of the alkalies, forming a yellow liquid; and a hot concentrated solution of it in ammo it cools, deposits a yellow crystalline compound. The pres a trace of a persalt of iron gives to esculetin a dark green but the colour is destroyed on the addition of an acid. A s of acetate of lead when mixed with one of esculetin, prod lemon-yellow precipitate ($C_{18}H_4Pb_2O_8$).

Fraxin ($C_{42}H_{22}O_{26}$) is a similar crystalline body obtaine the bark of the ash.

Cyclamin ($C_{40}H_{24}O_{20}$; Martius), from the *Cyclamen Eur* is another crystalline body, which splits into glucose and a r compound on boiling it with dilute acids.

(1308) SAPONIN ($C_{24}H_{20}O_{14}$?).—This substance is conta a considerable number of plants, including the *Saponaria offi* the *Polygala senega*, and the root of the common pink: it found in the pimpernel, in the fruit of the horse-chestnut, several varieties of *Lychnis*. Saponin is easily extracted, by of boiling alcohol (sp. gr. 0·840), from the root of the *Sapon* *soap-wort;* as the liquid cools the saponin is deposited as am phous sediment, which if coloured must be digested in et order to remove the colouring matter.

When dry, saponin forms a colourless friable mass, w destitute of odour, and of a sweetish, styptic, persistent tas applied to the mucous membrane of the nose it produces sneezing. Saponin is soluble in water in all proportions, y a somewhat opalescent liquid, which froths strongly on ag like a solution of soap, even though it may not contain than a thousandth of its weight of saponin; the liquid evaporated leaves the saponin in the form of a transparent, varnish. Its solution, or an infusion of soap-wort, is som employed instead of a solution of an alkaline soap, for cle the finer varieties of wool from grease. Saponin is also sol dilute alcohol, but insoluble in ether. Its solutions yield a precipitate with subacetate of lead.

When boiled with dilute acids saponin yields a peculiar acid, the *saponic* or *esculic*, and at the same time a substance resembling gum ($C_{12}H_{11}O_{11}$) is separated, (Rochleder and Schwarz). Saponic acid may also be obtained by digesting saponin in weak alkaline solutions. The composition of saponic acid is doubtful, but it presents well-marked characters. It is nearly insoluble in water and in ether, but is readily dissolved by alcohol, which deposits it in granular crystals. Its salts with potash, soda, and ammonia, are soluble in hot water, and the liquid on cooling sets into a jelly. A solution of these salts in dilute alcohol, sp. gr. 0·960, deposits them in pearly crystals. Saponic acid forms compounds with lime, baryta, copper, and lead, which are insoluble in water, but soluble in dilute alcohol.

(1309) A variety of other neutral crystallizable and often poisonous principles have been obtained from plants, many of which are used medicinally, but few of them have been minutely examined. It is probable that many of these bodies will prove to be identical with others already known, and many others will most likely be found to belong to the class of glucosides.

The following are some of these bodies:—

1. *Antiarin* ($C_{14}H_{10}O_5$), the poisonous principle of the *Upas antiar*, which when introduced into a wound causes vomiting, convulsions, and death. It crystallizes in pearly scales, soluble in alcohol, sparingly so in ether; 27 parts of boiling ether dissolve 1 part of antiarin.

2. *Daphnin*, from the bark of *Daphne mezereum*, forms colourless radiated needles, soluble in hot water, alcohol, and ether.

3. *Elaterin* ($C_{20}H_{14}O_5$) is the active principle of *Momordica elaterium*. It is a white silky crystalline powder, insoluble in water, but soluble in alcohol, ether, and the oils: when heated, it melts and sublimes.

4. *Gentianin*, the bitter principle of *Gentiana lutea*, crystallizes in yellow needles freely soluble in alcohol and in ether, sparingly soluble in cold water, more abundantly soluble in boiling water.

5. *Hesperidin* is a white, tasteless, crystallizable body extracted from the white spongy part of the rind of oranges and lemons.

6. *Picrotoxin* ($C_{10}H_6O_4$) is an intensely bitter substance to which *Cocculus indicus* owes its activity. It forms small colourless stellate needles soluble in 25 parts of boiling alcohol.

7. *Santonin* ($C_{30}H_{18}O_6$).—This substance possesses feebly acid properties; it is obtained from the seeds of several varieties of

[illegible] It is soluble in water and in alcohol. In [illegible] the seeds should be digested in alcohol with [illegible] of lime and santonin is dissolved, from wh [illegible] expelled by distillation, and on adding acetic [illegible] crystallizes.

[illegible] Colocynthin ($C_{56}H_{42}O_{23}$?) is a crystallizable bitter [illegible] ether, which is contained in the *Cucumis colo* [illegible] by boiling with acids is separated into glucos [illegible]

CHAPTER VIII.

COLOURING MATTERS.

[illegible] THE substances which are about to be treated [illegible] chapter under the head of *colouring matters,* are [illegible] on account of the similarity in the modes of [illegible] in the arts, and not from any well-marked chemi [illegible] which exist between them. The relations of many [illegible] to other groups are, however, remarkable, and prese [illegible] of considerable interest.

The colouring matters are found in all the organs of [illegible] madder, turmeric, and alkanet they are obtained f [illegible] in logwood, Brazil wood, and fustic they are foun [illegible] in quercitron in the bark; in safflower they are f [illegible] petals, and in saffron by the anthers of the flowers [illegible] Persian berry and in annatto they are obtained from [illegible]

[illegible] colouring matters in the form in which they exi [illegible] plant give little or no indication of their tinctoria [illegible] case with indigo, and with the blue colouring [illegible] lichens; but by the action of fermentation and [illegible] oxygen, or by the effect of ammonia, or by the [illegible] chemical agents, they may be made to furnish dye- [illegible] brilliancy and beauty.

[illegible] of the organic colouring matters fade or chan [illegible] the combined influence of oxygen and solar lig [illegible] species of slow combustion, and are in many ca [illegible] colourless. Many of them are also deprived of co [illegible] agents, such as sulphuretted hydrogen, the sulp [illegible] metals, and the salts of the protoxides of iro [illegible] these cases of deoxidation, the colouring matte it is again exposed to the air, recovers its original hue. The roots of the plant appear to exert a reducing effect upon many colouring matters, whilst in the flower the opposite effect takes place; this is beautifully shown in an experiment by Persoz:—if the roots of a transparent plant, such as balsam (*impatiens*), be immersed in a coloured solution, such as one of logwood, the coloured liquid is absorbed by the radicles, it is deprived of a portion of oxygen, and loses its colour; in this form it continues to circulate through the plant until it reaches the petals of the flowers, where it again absorbs oxygen and resumes its original hue.

All organic colouring matters are destroyed by chlorine, which acts in some cases by displacing hydrogen, in others by decomposing water and setting oxygen at liberty, and thus producing new compounds destitute of colour. Sulphurous acid also in many instances combines with the colouring body, and produces new compounds not possessed of tinctorial power.

Almost all the colouring matters require a preparation more or less elaborate before they are fit for use; many of the processes employed in brightening and fixing their tints are of a complex nature, and still retain their original empirical character. In many of the colouring matters of organic origin, nitrogen is an essential constituent, though in a still greater number it is absent. The colouring matters in most frequent use exhibit the properties of very feeble acids. The concentrated alkalies, especially in the presence of free oxygen, however, for the most part decompose them rapidly; but they are more soluble in dilute alkaline liquids than in pure water, and they form definite insoluble compounds with the earths, and with some metallic oxides, such as those of lead and of tin. Such compounds with the metallic oxides usually possess great tinctorial or colouring power, and are termed *lakes*. The formation of these insoluble compounds is a circumstance of fundamental importance to the dyer and calico-printer, since upon it depends the general method of *mordanting* (1343), used in the arts of dyeing and calico-printing.

(1311) YELLOW DYES.—The most important yellow dye-stuffs are quercitron, fustic, saffron, turmeric, annatto, and weld. The colouring matters of the Persian berries, of purree, and of rhubarb, are less frequently employed.

1. *Quercitron* is the bark of the *Quercus tinctoria*. It yields a yellow crystallizable principle, *quercitrin* (1304), of feebly acid properties, soluble in alcohol, sparingly so in water, freely so in alkalies.

2. The *Morus tinctoria*, or *Old fustic*, is particularly em-

ployed for dyeing woollens yellow; it is also used to im
them green and olive hues when mixed with indigo and salts
Fustic furnishes a yellow colouring matter, which may be o
in crystals by evaporating its aqueous infusion. This su
has been termed *moritannic acid* (1158) ($C_{36}H_{16}O_{20}$). It
bitter taste, is soluble in ether, and gives a green precipita
salts of iron. Acids and alkalies deepen the tint of the
solution without producing any precipitate. When mix
alum it produces no precipitate, but on the addition of ca
of potash to this solution, a yellow lake is formed.

3. The *Rhus cotinus*, or *Young fustic*, contains a d
yellow dye, which is very soluble in water; potash ren
purple, passing into a reddish yellow; while the acetates
and of copper produce an orange-coloured lake with a deco
this wood. Wool mordanted with alum acquires a bright
dye in a bath of this colouring principle.

4. The *Crocus sativus* yields *Saffron*, a colouring matt
tained in the anthers of the flower; it is very soluble in wa
in alcohol. It has been but imperfectly examined.

5. *Curcumin*, or the colouring matter of *Turmeric* (C
longa), is of a resinous nature; it is nearly insoluble in water,
dissolved freely by alcohol and by ether. Alkaline solutio
it up abundantly, and change the colour to brown. This
of colour is often employed in the laboratory to indic
presence of free alkali, since paper tinged yellow with tin
turmeric becomes brown when immersed in a solution co
uncombined alkali. Curcumin is soluble without change
in the acetic, phosphoric, hydrochloric, and sulphuric acids.
employed for dyeing wool and silk, as well as for colour
curry powder of India.

6. *Annatto.*—This colouring matter is in the form of
prepared from the seeds of the *Bixa orellana*, and is u
dyeing nankeen. It appears to contain an orange-red co
substance, called *bixin*, and a less important yellow one
orellin. Bixin is a resinous matter sparingly soluble in
but freely so in alcohol and in ether. The alkalies diss
producing a deep red colour, and on neutralizing the
with an acid it falls as an orange precipitate. The fixed
dissolve this colouring principle, which closely resembles
the turmeric.

7. The root of the common *Rhubarb* yields a yellow co
matter, termed *rhein* or *chrysophanic acid* ($C_{20}H_8O_6$?), w
also found in one of the lichens (*Parmelia parietina*).

ngly soluble in water, but freely soluble in the alkalies, pro- ng a reddish brown-coloured liquid, from which on the ad- n of acetic acid it may be precipitated in flocculi ; this change yellow to red is effected by a minute trace of alkali, so that r stained with rhubarb may be used as a test for the presence free alkali. Rhein is accompanied by a portion of resin, h may be precipitated by the addition of ether to the alcoholic tion. Chrysophanic acid is soluble in ether and in hot alcohol, which it may be obtained in crystals of a golden yellow llic lustre.

8. The *Weld* or *Reseda luteola* also furnishes a yellow colouring er, which is highly prized for its solidity and durability. *olin* ($C_{40}H_{14}O_6$; Moldenhauer), as this substance is termed, may stracted from the dried plant by means of boiling water; it is y soluble in alcohol, less so in ether, and but very sparingly ater. It may be sublimed unaltered, and condenses in yellow les. The alkalies, both caustic and carbonated, dissolve it dantly, and form deep yellow solutions. Cold sulphuric also dissolves it, and deposits it unaltered on dilution. Its ions yield yellow lakes with alum, protochloride of tin, and te of lead.

9. *Persian Berries.*—The fruit of various species of *Rhamnus*, gathered before it is fully ripe, contains a considerable nt of a yellow colouring matter, termed *chryso-rhamnin* $H_{11}O_{11}$?). This substance may be extracted by means of , which deposits it in brilliant stellate groups of golden w crystals; an alcoholic solution of this compound yields an alcoholic solution of acetate of lead a yellow lake (2 PbO, $_{11}O_{11}$?). Chryso-rhamnin is nearly insoluble in cold water, f boiled with water it is partially dissolved, and is converted a compound termed *xantho-rhamnin* ($C_{23}H_{12}O_{14}$?), which is one of the constituents of the ripe berries (Kane). Gellatly that xantho-rhamnin, like the glucosides, splits, when treated dilute acid, into a resin and glucose.

o. *Purree, or Indian Yellow.*—This substance has been parti- ly examined by Stenhouse and by Erdmann. It is a colour- atter highly esteemed by artists, and is supposed to be of l origin; it is sold in masses of three or four ounces in weight, have exteriorly a dark-brown colour, but when broken are bright orange-yellow. Its odour is peculiar, and resembles of castoreum. This substance consists chiefly of the mag- salt of a peculiar acid, termed *purreic* or *euxanthic* acid. e is scarcely soluble in water or in alcohol, but it is entirely soluble in boiling dilute hydrochloric, or in acetic acid ; a pale yellow needles of euxanthic acid ($HO,C_{42}H_{17}O_{21}$; are deposited in stellate groups. It is somewhat sc boiling water, and is readily dissolved by boiling alcobo ether. Cold water dissolves but very little of it ; alka tions dissolve it, and form a yellow liquid. A solution thate of potash when mixed with the solutions of the sa earths gives brilliant yellow sparingly soluble precipita acetate of lead it forms a yellow insoluble lake.

When euxanthic acid is heated in a small tube to a te a little above 212°, it melts, and a yellow sublimate of *pa euxanthone* ($C_{40}H_{12}O_{12}$) is formed, whilst water and car are evolved : it is also obtained by transmitting chlorin a hot solution of euxanthic acid in absolute alcohol ; and compound is produced when euxanthic acid is dissolved vitriol, the solution gradually depositing crystals of eu The sulphuric solution contains a new colligated aci *sulphohamathionic acid*, the composition of which is doul

The yellow dyes are not often used alone. They are employed in combination with other colours to modify to produce compound colours, as when mixed with blu duce green.

(1312) THE RED DYES are of greater importance ; madder, logwood, Brazil-wood, camwood, sandal-wood, cochineal, and lac dye, and the aniline dyes, are thos extensive use.

(1313) 1. MADDER is the root of the *Rubia tinctoru* which is grown largely in the Levant, in the South of F in Alsace. It is consumed in enormous quantities for d and purples ; Turkey red cloth owes its brilliant h colouring matter of this root. The composition of th root has been the subject of many chemical investig most recent and complete being those of Rochleder and

According to the microscopic observations of Dec madder root, whilst growing, does not contain any red matter ; but its cells are filled with a yellow substa increases in quantity with the age of the root ; and thi exposure to the air absorbs oxygen, after which the red developed ; an observation which agrees with the exper Higgin and of Schunck.

According to the last-named chemist, the madder ro merce, in addition to ligneous fibre, contains several dis stances ; viz., a bitter principle, rubian,—which by its d tion yields two colouring matters, *alizarin* and *rubiacin*,—two resins, pectic acid, and a brown substance which is probably a product of oxidation of some of the foregoing bodies. It also contains oxalate and phosphate of lime, besides other saline matters.

Some of these bodies are injurious to the brilliancy of the dye. Alizarin, according to Schunck, is the only true dyeing principle of the madder root. It has already been stated that alizarin does not exist ready formed in the growing root, but that it is produced by the decomposition of rubian; and it is well known to the dyer that the full colouring power of the root is not developed until after the dye-stuff has undergone partial fermentation.

In order to extract the whole of the colouring material, Schunck dissolves out the soluble matter from the root with water, and decomposes this solution by boiling it with dilute acid, when the whole of the colour-giving portion, including the alizarin, is precipitated. If this precipitate be boiled with water, the alizarin is dissolved, and the rubiacin and the resins are left. Another plan of obtaining alizarin consists in reducing the root to a coarse powder, treating it with hot sulphuric acid, and well washing it till the last traces of acid are removed; the earthy matters are thus rendered soluble, and everything which water will take up is removed; but nearly the whole of the alizarin remains untouched, since it is insoluble in water containing free acid; the undissolved mass when dried is largely used in the print-works under the name of *garancin.* By boiling this garancin in a large quantity of water, the colouring matter is dissolved, and on adding sulphuric acid it is precipitated mixed with several impurities. If this precipitate be well washed, dried, and submitted to sublimation, beautiful orange-coloured needles of alizarin are obtained; these, if washed with cold alcohol and dried, are perfectly pure.

(1314) *Alizarin* ($C_{14}H_5O_4+3$ Aq, Schunck; $C_{20}H_6O_6+4$ Aq, Strecker).—This is a red crystalline matter destitute of odour and of taste; it is neutral to test-papers, and is almost insoluble in cold water. It is but sparingly soluble in hot water; hot alcohol dissolves it more freely, and if this solution be evaporated, alizarin is deposited in plates resembling those of Mosaic gold. It is also soluble in ether; acids brighten its tint but do not dissolve it. Potash dissolves it freely, and strikes a beautiful purple; but it is precipitated unaltered on adding an acid; with lime, baryta, and oxide of iron, it forms insoluble purple lakes. With alumina it forms a beautiful red lake. Alizarin is not decomposed even by boiling sulphuric acid, which dissolves it, and on dilution deposits it unchanged. Boiling *dilute* nitric acid converts alizarin into

phthalic (alizaric) acid, and probably into oxalic acid (St
and Wolff), whilst nitrous vapours are evolved :—

$$\overbrace{C_{20}H_6O_6}^{\text{Alizarin.}}+H_2O_2+2\,O_4=2\,\overbrace{HO,C_{16}H_4O_6}^{\text{Phthalic acid.}}+2\,\overbrace{HO,C_4O_6}^{\text{Oxalic acid.}}$$

The crystals of alizarin deposited from its spirituous or aq
solution lose about 18 per cent. of water at 212°. By a h
about 420° alizarin is sublimed, but part of it undergoes d
position. The sublimate forms beautiful transparent o
coloured needles, which are anhydrous and of high lustre.

(1315) *Rubian* ($C_{56}H_{34}O_{30}$? Schunck); the *Ruberythric A*
Rochleder ?—This is a bitter uncrystallizable principle,
under the influence of acids, of alkalies, and of a peculiar a
ferment (*Erythrozym*) contained in the madder root, is brok
into a fermentable sugar, and into alizarin and other col
matters. Synaptase produces a similar decomposition of ru

The preparation of rubian in a state of purity is not
Schunck takes advantage of its tendency to contract a sup
combination with charcoal, and recommends that ground m
be digested in hot water (1 lb. of madder to a gallon of w
that the undissolved portion be strained off, and that to
gallon of the hot liquid an ounce of bone-charcoal be added.
mixture after brisk agitation is to be allowed to settle, a
charcoal collected on a filter and washed with cold water, un
washings no longer become green when heated with hydro
acid. The charcoal which has been thus treated has become sat
with rubian ; it is next to be boiled with alcohol, and this tre
is to be repeated so long as fresh alcohol acquires a yellow
when boiled with the charcoal. The alcoholic solutions on
ration yield rubian, contaminated with a variable amount of
and with a green colouring matter : this colouring matter
however, be got rid of by treating a solution of the rubian in
a second time with charcoal, and repeating the entire process
alcoholic solution when evaporated leaves the rubian in th
of a brittle transparent mass of a dark yellow colour, rese
dried gum or varnish.* It is not deliquescent, but is abun

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* Rochleder's ruberythric acid was obtained in crystals from an
of madder by separating the alizarin and other colouring matters b
of neutral acetate of lead, and then precipitating the rubian with su
of lead, decomposing this precipitate with sulphuretted hydrogen, and
the sulphide of lead with alcohol (the rubian accompanies the sul
lead). The rubian is dissolved by the alcohol, and is to be combin
baryta, dissolved in dilute acetic acid, re-precipitated by subacetate
and again treated with sulphuretted hydrogen after the lead precip

le in water, less freely so in alcohol, and insoluble in ether.
n heated to about 266° it melts, swells up, disengages water,
gives off orange vapours of alizarin, leaving a bulky carbo-
ous residue.

Solutions of rubian are of a pale yellow colour; they are not
cipitated by the metallic salts generally, but if mixed with sub-
ate of lead an insoluble compound is formed. Alkalies change
olour of a solution of rubian into blood red; but, if they be
wards neutralized by the addition of an acid, the yellow tint
restored: if, however, the alkaline liquid be boiled, its colour
nges to purple, and on the addition of an acid red flocculi are
cipitated. Oil of vitriol forms a blood-red solution with rubian.
ld nitric acid has little action upon rubian, but when heated
h it, red nitrous fumes are evolved, and *alizaric* (phthalic) acid
72) is found in the liquid.

If a solution of rubian be boiled with dilute sulphuric or
lrochloric acid, orange-coloured flocculi are precipitated, and
uncrystallizable sugar remains in the liquid. These coloured
uli consist of alizarin, rubianin, and two resins. For the
de of separating these bodies, the reader is referred to Schunck's
er (*Phil. Trans.* 1851, p. 445).

Rubianin ($C_{44}H_{24}O_{20}$?) is deposited from its solution in boiling
hol in silky lemon-yellow crystals, which are soluble in boiling
er. Oil of vitriol dissolves it with a yellow colour; on the
lication of heat to this solution it becomes blackened, and
ves sulphurous acid. Nitric acid dissolves but does not de-
pose it.

Rubiacin ($C_{32}H_{11}O_{10}$? Schunck) is one of the components of
mercial madder; it assumes the form of beautiful orange
ured tables, or of brilliant yellow needles, resembling those of
ide of lead. It is sparingly soluble in boiling water, but is
dily dissolved in alcohol; it may with ease be sublimed un-
red. Rubiacin is a compound of considerable stability; its
tion in oil of vitriol may be boiled without undergoing decom-
ition. Hydrate of alumina acquires an orange tint when
ated with an alcoholic solution of rubiacin.

When rubiacin is dissolved in a solution of perchloride or per-
ate of iron it gives a brownish-red liquid, which on the addi-
an acid deposits flocculi of *rubiacic acid* ($HO,C_{32}H_8O_{16}$?).
y is dissolved by the alkalies with a purple colour.

---

d through alcohol. On evaporation of the alcoholic solution
acid is left in crystals ($C_{72}H_{40}O_{14}$?). Schunck considers this body
lt of the *decomposition of rubian*, and not rubian itself.

For further details, the reader is referred to the pa Schunck, Liebig's *Annal.* lxvi. 175; *Phil. Trans.* 1851, 1855; and of Rochleder, Liebig's *Annal.* lxxx. 321, lxxxii.

(1316) 2. Logwood.—This valuable dye-stuff is exte employed for dyeing black with alum, but acids change the to red. It is the produce of the *Hæmatoxylon Campech* It contains a crystalline matter termed *hæmatoxylin* (C_{32}H 2 Aq and 6 Aq; Gerhardt), which, however, in its pure not red, but straw-yellow or honey-yellow. Under the co influence of the alkalies and oxygen it assumes an intens colour. In order to obtain hæmatoxylin, powdered com extract of logwood mixed with quartzose sand (to prevent agglomerating into masses) is digested for several days wi or six times its volume of ether. The liquid is distilled acquires the consistence of syrup; it is then mixed with and set aside in a vessel loosely covered. In the course days the hæmatoxylin is deposited in crystals. Extract wood, when thus treated yields from one-eighth to one-tent weight of this substance.

The crystals of hæmatoxylin are transparent, and co long, yellow, brilliant four-sided needles: these crystals six equivalents of water, which they lose at 212°. If a of hæmatoxylin saturated at the boiling point be allowed in a closed vessel, granular crystals with 2 Aq are de Hæmatoxylin has a sweet taste, free from astringency, like liquorice. It is sparingly soluble in cold water, but readil boiling water. Ether and alcohol dissolve it freely.

Solution of acetate of lead gives in one of hæmatoxylin precipitate, which speedily becomes blue; salts of copper dirty green precipitate, which also quickly becomes blue; of barium occasions a red precipitate; protochloride of tin rose-coloured lake, and iron alum a scanty blackish violet tate; ordinary alum gives a red solution, but does not any precipitate. A deep blue-black ink may be prepared by dissolving 120 grains of commercial extract of logwood in a water, and adding 15 grains of chromate of potash, but it soo

Sulphuric and hydrochloric acids have but little effe hæmatoxylin, but diluted nitric acid colours it red. Conce nitric acid converts it into oxalic acid.

Solution of potash communicates a violet tint to one of toxylin, and if the air have access to the solution, th becomes first blue and then brown, whilst oxygen is ab Solutions of hæmatoxylin are not altered by exposure to the solution furnishes an exceedingly delicate test of the pre- of ammonia or its carbonate, in which case the liquid acquires ple tint, whilst oxygen is absorbed, and hæmateate of ammonia med, and may be obtained abundantly by an addition of onia :—

$$\underbrace{2\,C_{32}H_{14}O_{12}}_{\text{Hæmatoxylin.}}+O_4+4\,H_3N=2\,H_2O_2+2\,(\underbrace{2\,H_3N,C_{32}H_{12}O_{12}}_{\text{Hæmateate of ammonia.}}).$$

mmonia may be removed from this compound by means of acid, when the *hæmatein* ($C_{32}H_{12}O_{12}$) is precipitated in inous red flocculi, resembling hydrated peroxide of iron. tein is sparingly soluble in cold water, but is more readily in boiling water, and the solution on evaporation yields a ed mass of green crystals with a metallic lustre. Sul- ted hydrogen combines with hæmatein when transmitted h its solution, and deprives it of its colour; the solution by re to air loses the sulphuretted hydrogen, and deposits red hæmatein.

tash dissolves hæmatein with a blue colour, which becomes when exposed to the air. Its ammoniacal solution is of a rple, which also becomes brown on exposure. Hæmateate onia yields coloured precipitates with many metallic salts; etate of lead it gives a deep blue, with sulphate of copper blue, with protochloride of tin a violet, and with iron alum precipitate.

17) 3. Brazil-wood is the produce of the *Cæsalpinia ensis*. It yields by treatment with alcohol yellow or orange of *brezilin*, which are likewise soluble in water and in ether. specially the citric, give it a bright yellow colour; with alka- ives a violet or purple colour: hence it is sometimes used t of the presence of alkali in a free state. It absorbs oxygen he influence of ammonia, with which it forms a definite nd, analogous to that obtained by similar means from log- Brezilin forms, in combination with alumina, the basis of Like hæmatoxylin, it is bleached by nascent hydrogen sulphuretted hydrogen. *Sapan-wood* and *camwood* are o yield the same colouring principle as Brazil-wood. The of these red woods, though brilliant, is not very per-

dal-wood, *alkanet root*, and some other substances also ed dyes, but in general the vegetable red colours are . The colouring matter of alkanet is soluble in oils.

18) 4. Safflower is obtained from the petals of the *Car- tinctorius*. These petals contain two colouring principles,

one of which is yellow and soluble in water, but is of the dyer: it is a weak acid, of a bitter taste. If an safflower be mixed with an acetic solution of acetate soluble yellow salt of lead is formed, from which, on t of ammonia, a subsalt is precipitated in dark yellow fl

The really valuable colouring principle of the saffl and is employed in the preparation of *pink saucers* for for imparting a beautiful and brilliant rose-red to silk; quickly when exposed to the sun's light.

Carthamin ($C_{28}H_{16}O_{14}$), as this substance is termed, in water and in acids, but is easily dissolved by the a adding an acid to the solution it is again precipitated soluble in alcohol. Carthamin may be obtained b safflower in weak acetic acid, in order to remove the stuff; the washed dye is next digested in a solution c of soda; a skein of cotton is then placed in the liquid, juice, or a solution of citric acid, is added. The cotto chanically removes the flocculent precipitate of cart the liquid; the yarn must be washed with cold water, ing matter again dissolved by carbonate of soda, and re by the addition of citric acid. Carthamin when dr pulverulent substance; it has a greyish metallic l viewed in mass, but in thin layers it is of a beautif red. Its solutions in alkalies gradually absorb oxygen altered.

(1319) 5. Carmine is contained in the *Coccus cact* colouring matter of the cochineal. After treating th insects with ether to remove the fat, the insoluble digested in water, and on adding acetate of lead, a l precipitated of a purple colour. This must be well composed by sulphuretted hydrogen, and the filtere evaporated to dryness *in vacuo* over sulphuric acid. finds the colouring matter of the cochineal thus obtaine acid body, which he terms *carminic acid* ($C_{28}H_{14}O_{1}$) purple brown, friable mass, soluble in all proportions and in water, but very slightly soluble in ether; it n solved unchanged in strong sulphuric and hydrochl Nitric acid even if dilute decomposes it; chlorine, i bromine also decompose it, and change its colour to yel fixed alkalies change the colour of the aqueous solution the alkaline earths give purple precipitates; with alum produced till ammonia is added, when it falls as a beautif precipitate. The lakes, with acetate of lead, and wit r, zinc, and silver, are purple; with salts of tin a bright on solution is obtained.

hen carminic acid is treated with dilute nitric acid it yields id of a yellow colour, which crystallizes in rhombic plates; ery soluble in boiling water, in alcohol, and in ether. It med *nitrococcussic acid* ($2\,HO,C_{16}H_3(NO_4)_3O + 2\,Aq$), and is ric with trinitranisic acid. It deflagrates strongly when l. Its salts are soluble in water, and most of them are also lved by alcohol. Cochineal is extensively employed, in combion with oxide of tin, as a scarlet dye for cloth.

6. LAC DYE is very similar to cochineal in its nature, being rnished by a species of coccus. Of late years this dye-stuff been extensively substituted for the more costly cochineal, it furnishes scarlets equally vivid, and even more permanent, the pinks are not so good. In dyeing scarlets the liquid loyed for dissolving the colouring matter is a solution of tin ncentrated hydrochloric acid, 20lb. of acid being required for pound of tin; the dye-stuff is digested in an equal weight of liquid, and the cloth, after being cleansed by boiling with fuller's h, is introduced into a bath containing a *mordant* composed of ution of protochloride of tin, prepared by gradually dissolving of tin in a mixture of 27lb. of hydrochloric acid, and 1½lb. of acid (sp. gr. 1·19). In order to dye 100lb. of cloth, the wing process, according to Ure, is adopted:—300 gallons of r are raised to 150° in a tin boiler, and 1½lb. of solution of nordant and a handful of bran are added; when the liquor it is skimmed, and 10½lb. of lac dye previously dissolved in acid, and 23½lb. of mordant, are introduced; immediately which 10½lb. of bitartrate of potash, and 4lb. of ground ch are suspended in a bag in the bath for five minutes, and withdrawn; the fire is now extinguished, and 20 gallons of water containing 10lb. more of tin mordant are added, after the cloth is introduced; the liquid is then boiled for an and at the end of that time the cloth is withdrawn and well l.

320) 7. EXTRACT OF ALOES.—This substance may, by the of nitric acid, be made to yield various compounds, which of being fixed by means of mordants upon silken and woollen o which they impart dyes of great durability and beauty. of aloes contains a compound termed *aloin*, which is th in water and in alcohol; when exposed to the air oxygen, and becomes of an intense red colour.

$C_{34}H_{18}O_{14}$? Stenhouse).—In order to extract this sub-

stance, powdered Barbadoes aloes, mixed with sand to prev
particles from agglomerating, are treated with cold wat
dark liquid thus obtained, if evaporated *in vacuo* to the con
of syrup, and left for a few days in a cool place, deposits g
crystals, which are more or less deeply coloured: these
pressed between folds of blotting paper, and recrystalliz
water, the temperature of which is not to exceed 150°. Al
also be obtained in crystals from a warm alcoholic solution, i
of pale yellow needles. Cape aloes and Socotrine aloes a
tain aloin, but it is accompanied by a large proportion of
matters, which interfere with its crystallization. Alo
neutral substance, with a sweetish, intensely bitter, persiste
It constitutes the purgative ingredient in aloes. At a
ture of 212° it is rapidly altered; at 300° it melts, and
strongly in the open air it burns with a smoky flame. The
both caustic and carbonated, dissolve it readily, forming
coloured solutions.

When extract of aloes is treated with nitric acid
Chrysammic acid ($HO,C_{14}H(NO_4)_2O_3$?). This compou
tained by treating extract of aloes for some days with 8
weight of nitric acid (sp. gr. 1·37), distilling off the gre
of the acid, and then adding water; chrysammic acid is
tated. It is nearly insoluble in water, but soluble in alc
in ether, from which it may be obtained in golden yellow
on the application of heat it is decomposed with explosi
salts are soluble in hot water and form deep red s
most of them may be crystallized, and the crystals
metallic lustre. Ammonia dissolves the acid with the f
of a beautiful purple-coloured solution, from which, on the
of a neutral salt, such as nitrate of potash, an amidated c
is deposited in brilliant dark green needles, which exert a p
action upon light which is transmitted through them.

Schunck finds other acids in the mother liquor fro
the chrysammic acid has been separated; one of these,
chrysolepic acid, appears to be identical with carbazotic a
other resinoid acids, the *aloetic* [$HO,C_{14}H_2(NO_4)_2O+Aq$
aloeretinic, are also formed at the same time: they hav
tensely bitter taste, and form red salts.

(1321) BLUE DYES.—1. INDIGO.—The most importan
blue colouring matters, and the one which has been most ac
studied, is indigo, which is chiefly obtained from the
various species of the *Indigofera*. Crude indigo contains

colouring material, termed *indigotin*, or indigo blue, from which numerous derivatives belonging to the indigo series have been prepared. Such of them as contain nitrogen have hitherto been procured from natural indigo only, but by the metamorphosis of these azotised compounds, bodies of a less complicated order have been obtained, many of which belong to the salicylic, the quinic, and the phenic groups. The following are the most important of the immediate derivatives of indigo: if indigo blue be described under the term *indyl*, their relations to it will then be represented by the formulæ of the fourth column:—

Indigo blue	$C_{16}H_5NO_2 =$	Indyl	In
White indigo	$C_{16}H_6NO_2 =$	Hydride of indyl	In,H
Isatin	$C_{16}H_5NO_4 =$	Oxide of indyl .	In,O_2
Isatic acid	$HO,C_{16}H_6NO_5 =$		HO,In,H,O_3
Isathyd	$C_{16}H_6NO_4 =$	Oxide of indyl and of hydrogen . .	$\left.\begin{matrix}In\\H\end{matrix}\right\}O_2$
Indin	$C_{32}H_{10}N_2O_4 =$	Polymeride of indyl	In_2
Hydrindin	$C_{32}H_{11}N_2O_4 =$	Hydride of indin	$In_2,H.$

(1322) *Condition of Indigo in the Plant.*—Indigo is extracted from the leaves of a variety of plants, principally the produce of India and America: it is especially obtained from the various kinds of *Indigofera*. The produce of the *Indigofera anil* was particularly examined by Chevreul: the *Isatis tinctoria*, or common woad, and several other plants, also yield indigo in small quantity, and it has been stated to occur occasionally in the milk of cows, and in human urine; so that indigo may be produced under circumstances apparently widely different.

The blue colouring matter of indigo is not soluble in water or in alkaline leys, but by treatment with deoxidizing agents in contact with water, it may be made to combine with an additional equivalent of hydrogen, and produce a white substance termed *reduced indigo*, which is also insoluble in water, but is soluble in alkaline leys. When an alkaline solution of this reduced indigo is exposed to the air it absorbs oxygen, and is converted into indigo blue, which is precipitated in the insoluble form.

In their growing state, the plants which yield indigo give no evidence of its presence, the juice being of a yellow colour. Chevreul supposes that the indigo exists in the plant in the reduced form; but, as Schunck has shown, this view is erroneous, since the juice of the plant is always acid, and reduced indigo requires an alkaline liquid for its solution. Moreover, as soon as such a solution is exposed to the air it becomes blue, and this is not the case with the juice of the *Indigofera*. Schunck has recently made the question of the condition in which indigo is contained in these plants the subject of a special inquiry; and although at present his experiments have only been conducted upon the woad, or *Isatis tinctoria,* which may be readily cultivated in this country, the results which he has obtained possess considerable value and interest [*Manchester Memoirs* (1855), vol. xii. p. 177]. From these experiments he concludes, that the woad does not contain indigo ready formed either in the blue or in the colourless state; that the indigo-producing substance is soluble in water; and that the formation of the blue colouring matter in watery extracts of the plant is neither caused nor promoted by the action of oxygen or of the alkalies, but that the plant contains a peculiar principle, which he terms *Indican* ($C_{52}H_{33}NO_{36}$?). This body, by its decomposition, yields indigo. He found that, when heated with sulphuric or hydrochloric acid, it was decomposed; indigo blue, indigo red, and a particular species of sugar, *Indiglucin* ($C_{12}H_{10}O_{12}$), were formed.

$$\overbrace{C_{52}H_{33}NO_{36}}^{\text{Indican.}}+H_2O_2=\overbrace{C_{16}H_5NO_2}^{\text{Indigo blue.}}+3\,\overbrace{C_{12}H_{10}O_{12}}^{\text{Indiglucin.}}.$$

Indican is a yellow, transparent, amorphous substance; it is very deliquescent, and is also soluble in alcohol and in ether. It has a slightly bitter, nauseous taste; when boiled with caustic alkalies it evolves ammonia. A solution of indican becomes of a bright yellow colour when mixed with alkalies, or with lime or baryta. Acetate of lead occasions a sulphur yellow precipitate in its alcoholic solution, but none in its aqueous solution till ammonia has been added. Solutions of indican must be evaporated without the application of heat, for if its aqueous solution be heated it undergoes a complete change; the elements of water are assimilated, and a substance is obtained which is not soluble in ether, and is dissolved but in small quantity by alcohol: the aqueous solution of this new body does not form indigo blue when boiled with acids, but it yields black flocculi consisting of two compounds; one of which is a resinous substance, fusible in boiling water, and the other a humus-like compound, which Schunck considers to be identical with the *indigo brown* of Berzelius. These observations show how important it is to avoid the use of boiling water in the preparation of indigo on the large scale. Solutions of indican which have been mixed with alkalies, and then boiled with acids, yield no indigo blue, but a mixture of this humus-like body and resin.

Extraction of Indigo.—If the dried leaves of the *Indigofera* be digested in cold water for some hours, a green solution is obtained, which when exposed to the air undergoes fermentation, during

indigo is separated in the form of a blue sediment. The
of preparing indigo, usually adopted in the East Indies, is
l to be the following:—the green plants, cut during the
hs of June and July, just before flowering time, are placed in
en or brick troughs of about twenty feet square and four or five
leep, the plants are then submitted to moderate pressure and
red with water; after the lapse of a few hours a sort of fer-
ation takes place in the mixture, which is allowed to continue
om twelve to fourteen hours; ammonia and carbonic acid are
gaged, the temperature rises to 100° or 110°, and the
d in the troughs becomes covered with a blue, iridescent film.
he fermentation proceed too far the colouring matter is de-
yed; when the process has reached a certain point, of which
manufacturer judges by experience, the liquid acquires a sherry
e colour, it is then drawn off into other troughs, where, on
kly agitating with oars, the pigment is separated as a deep
granular powder. The supernatant liquor is run off; the
ment, with a portion of the liquid, is heated to the boiling point;
pasty mass is then drained on calico, pressed, cut into cakes,
dried.

The indigo of commerce is by no means a homogeneous body.
most important constituent is *indigotin*, or indigo blue, but it
ains several other substances, and in particular two bodies,
n as *indigo brown* and *indigo red*. The brown colouring
er is soluble in potash: the indigo red may be extracted by
ns of boiling alcohol.

(1323) *Indigo blue* or *Indigotin* ($C_{16}H_5NO_2=131$) may be sepa-
from these impurities by the process of sublimation. If a
quantity of indigo be heated between two watch-glasses so
protect it from the air, a considerable proportion of it is
posed, but a portion is sublimed, and becomes condensed in
copper-coloured six-sided crystals upon the surface of the
operated on. Pure indigo blue is, however, obtained more
dantly by the following plan contrived by Fritsche:—4 ounces
mercial indigo in fine powder, and 4 ounces of grape sugar,
laced in a flask capable of containing 10 pints of liquid; 6
s of a saturated solution of caustic soda are then added, and
flask is filled up with boiling alcohol; it is then closed so
prevent the access of air, and the mixture after agitation is
ide. In a few hours it becomes clear; the yellowish red
is then drawn off with a syphon, and if left exposed in
els it rapidly absorbs oxygen, becomes brown, and depo-
s, which *after being treated* first with alcohol, and then

with hot water, and dried, form perfectly pure indigo blue. Good indigo yields nearly half its weight of crystallized indigo blue.

Indigotin fuses at about 550°, and furnishes purple vapours. Amongst the products of its destructive distillation are hydrocyanate and carbonate of ammonia, aniline, and a peculiar empyreumatic oil. Indigo blue is metameric with cyanide of benzoyl. It is insoluble in water, alcohol, ether, and the fixed and volatile oils, as well as in dilute acids and alkalies.

(1324) *Compounds of Indigo with Sulphuric Acid.*—Sulphuric acid appears to form several compounds with indigo; two of them have been analysed, viz., the *sulphindylic*, or *sulphindigotic* acid, and the *sulphopurpuric*, or *sulphophenicic acid;* a third acid, the *hyposulphindigotic*, appears also to be produced along with the foregoing acids.

Sulphindylic Acid ($HO,C_{16}H_4NO,S_2O_6$).—When commercial indigo is triturated with 6 times its weight of fuming sulphuric acid, considerable heat is developed, and a blue solution is formed, which is extensively used for dyeing cloth, under the name of *Saxony blue.* Ordinary oil of vitriol may also be employed to dissolve indigo, but more than double the quantity of such acid is required, and it must be heated to 130° or 140°. If a sufficient amount of acid be employed, almost the whole of the indigo may be dissolved, and if the liquid be allowed to stand for a few hours, it will remain clear on being diluted. The filtered liquid contains a mixture of sulphindylic and hyposulphindigotic acids. If the original acid liquid be diluted with from thirty to fifty times its bulk of water, and flannel which has been washed with soap and carbonate of soda, and then with water, be immersed in the liquid, the indigo acids will attach themselves to the flannel, leaving the excess of sulphuric acid in the mother liquor. The colouring matter may be entirely removed from the flannel by digesting it in a dilute solution of carbonate of ammonia: a deep blue liquid is thus obtained, which when evaporated to dryness and treated with alcohol, is separated into sulphindylate of ammonia, which is insoluble, and hyposulphindigotate of ammonia, which is dissolved by the alcohol.

Sulphindylate of potash ($KO,C_{16}H_4NO,S_2O_6$) is sparingly soluble in cold water, and is precipitated in flocculi, when acetate of potash is added to a crude solution of indigo in sulphuric acid, after dilution with 10 parts of water. The sulphindylates form blue solutions, which appear red when held between the eye and the sun. These solutions are rendered colourless by the action of reducing agents, but regain their blue colour by exposure to the air.

lphopurpuric Acid ($2\ C_{16}H_5NO_2,S_2O_6=HO,C_{32}H_9N_2O_3,S_2O_6$).
constitutes the greater part of the insoluble residue which
upon the filter when indigo is treated with a proportion of
ric acid too small to dissolve it wholly. It is insoluble in
containing free acid; but it forms a blue solution in pure
When acetate of potash is added to this liquid it gives a
precipitate of sulphopurpurate of potash.

325) *Reduced Indigo, White Indigo,* or *Indigogen* ($C_{16}H_6NO_2$).
en blue indigo is treated with deoxidizing agents, such as a
re of protosulphate of iron and potash, a yellow solution is
l, containing *reduced* indigo, a compound in which 1 equi-
more of hydrogen is present than in blue indigo. On
lizing the alkaline liquid by acetic acid, the reduced indigo
in dirty white flocculi, which are insoluble in water, but
ly soluble in alcohol and in ether; even when dry they
ally absorb oxygen from the air, but the absorption is much
rapid when moist, water and indigo blue being reproduced.
dilute acids are without effect upon reduced indigo; but
g sulphuric acid dissolves it, forming a deep purple liquid,
if diluted with water becomes blue, and is converted into
indylic acid. The alkaline solutions of reduced indigo are
itated by many of the solutions of the metallic salts, and
ompounds thus formed speedily become blue by exposure to
r.

he reduction of indigo from the blue to the white form may
ected by several processes :—

. By means of sugar as already described (1323).

. By the action of a mixture of protosulphate of iron and some
. Advantage is taken of this in the preparation of the
bath for dyeing purposes. The *copperas vat,* as it is
d, is employed in dyeing cottons and linen goods. The
rtions to be used will vary with the quality of the indigo,
r laboratory purposes the following ingredients may be em-
l :—1 part of powdered indigo, 2 of sulphate of iron, 3 of
lime, and 150 or 200 of water. The reaction is somewhat
icated; the lime acting on the sulphate of iron sets free
ed protoxide of iron, and this oxide in the presence of water
up an additional quantity of oxygen, becoming converted
he hydrated peroxide, whilst the liberated hydrogen unites
he indigo blue, and constitutes reduced indigo, which becomes
by the excess of lime, forming a yellow solution :—

$$,S_2O_6+2\ (CaO,HO)=2\ CaO,S_2O_6+2\ (FeO,HO), \text{ and}$$

$$4(FeO,HO)+H_2O_2+2\overbrace{C_{16}H_5NO_2}^{\text{Indigo blue.}}=2(Fe_2O_3,2\,HO)+2\overbrace{C_{16}H_6NO_2}^{\text{White indigo.}}$$

If the alkaline liquid thus obtained be exposed to the air, it becomes covered with a blue film, and deposits nearly pure indigo, and if mixed with hydrochloric acid, in vessels filled with carbonic acid, white indigo is obtained. If yarn or woven goods be immersed in such a solution, and then exposed to the air, the reduced indigo rapidly absorbs oxygen, and becomes converted into blue indigo within the fibres of the tissue, with which it contracts an intimate adhesion. The blue dye thus obtained is very intense and permanent, since it is insoluble in all ordinary solvents.

3. By means of orpiment and protochloride of tin, which are sometimes substituted in calico printing, as reducing agents in the place of the protosulphate of iron; in this case potash is employed instead of lime water as the solvent of the reduced indigo.

4. By means of decaying vegetable matter, which answers the same purpose as the sulphate of iron. This vat is chiefly used for dyeing yarns, and is prepared by some manufacturers in the following manner:—4 parts of finely powdered indigo, 50 of woad, 2 of madder, and 2 of carbonate of potash, are mixed with 2000 of water, and the mixture is kept for some hours at a temperature of about 194°; 1⅓ part of recently slaked lime is then added in small quantities at a time, after which fermentation commences; formic, acetic, and carbonic acids are formed, as well as ammonia. The lime reduces the carbonate of potash to the caustic state, and enables it to dissolve the indigo which has been reduced during fermentation by the decomposition of the vegetable matter. The addition of the lime is attended with the further advantage of precipitating a portion of brown colouring matter that would otherwise deaden the tint of the goods. The foam or *flower* of the vat has a beautiful blue iridescent appearance caused by reoxidation of the indigo at the surface, but the liquid beneath is of a deep yellow colour; by exposure to air it becomes green, and finally deposits blue indigo. To prevent this reoxidation the vats are kept covered when not in actual use; and fresh materials are added from time to time in order to maintain the liquor at a uniform strength.

Starch, sugar, bran, and other vegetable matters may be substituted for the madder and the woad in the indigo vat. These substances undergo fermentation, and act as deoxidizing agents; probably lactic and butyric acids are generated, and the indigo ines with the hydrogen, while the latter is in the act of being ted.

326) *Assay of Indigo.*—The quality of commercial indigo greatly ; the purest specimens usually occur in small masses intense violet-blue colour, which by friction with a hard th body acquire a coppery lustre. The best kinds are suffi- ly light to float upon water, and when broken they do not in cavities which exhibit brown or whitish veins. Indigo is, ver, frequently adulterated with sand, with starch, and some- it is said, with powdered lead. Good indigo should not more than from 5 to 8 per cent. of ash, calculated upon the mass ; during drying it loses from 5 to 8 per cent. of Starch may be detected by treating the indigo with boiling very faintly alkalized, and, after neutralizing the filtrate, ing it with iodine.

A simple method of determining the relative value of any ple of indigo, has been proposed by Bolley, who estimates its torial power by measuring the amount of a standard solution hlorate of potash, which is required to destroy the blue colour given sample :—10 grains of the indigo for assay are reduced very fine powder, and triturated with 2 fluid drachms of ing sulphuric acid ; the mixture is allowed to digest for twelve in a closed vessel with occasional agitation. The indigo be completely dissolved before the next part of the process is menced. As soon as the solution is effected, the liquid is to poured into a capsule with about a pint of water, containing unce of pure hydrochloric acid, and the mixture is brought to boiling point. A solution of chlorate of potash containing grains of the salt in 1000 grains of water, is then to be added e boiling liquid from an ordinary alkalimeter, drop by drop; the colour first becomes green, then greenish-brown, and when last tinge of green disappears and has been replaced by a ish-brown, the operation is complete. The number of divi- of the liquid required does not indicate the percentage of go blue, but simply the relative value of the different samples pared together.

Penny substitutes bichromate of potash for the chlorate; 100 of pure indigo blue requiring exactly 75 of the bichromate for oration : by this means an exact determination of the amount o blue may be effected.

1327) *Products of the Oxidation of Indigo.*—The action of g agents upon indigo gives rise to several interesting pro- *Concentrated chromic acid* breaks up the constituent

molecule of indigo, and occasions a copious disengagement of
bonic acid; but if a more dilute solution of chromic ac
employed, the indigo is converted into *isatin:* a similar cha
effected by the action of dilute nitric acid :—

$$2\,\overbrace{C_{16}H_5NO_2}^{\text{Indigo blue.}}+O_4=2\,\overbrace{C_{16}H_5NO_4}^{\text{Isatin.}}.$$

The oxidizing action proceeds further if the indigo be t
with nitric acid in a more concentrated form; thus, if indi
boiled with fuming nitric acid diluted with 10 or 12
of water, indigotic, or nitro-salicylic acid is formed (HO,
NO_4,O_5; 1270); and by a prolonged action of the nitric
carbazotic acid ($HO,C_{12}H_2(NO_4)_3O$; 1367) is produced;
these compounds contain less carbon than the true indigo
and this carbon is probably separated in the form of carboni
oxalic acid.

The oxidizing effect of hydrate of potash upon indigo is
what different from that of nitric acid. If indigo in fine pow
boiled with a solution of potash (of sp. gr. 1·36), it is dis
without the extrication of gas, and an orange-coloured li
formed, which on cooling deposits yellow crystals. If
crystals be dissolved in water, and treated with an excess of
chloric acid, a dirty bluish-red precipitate is formed; thi
stance constitutes Fritsche's *chrysanilic* acid, but accordi
Gerhardt, the precipitate consists of a mixture of reduced
with isatin, and the chemist last named represents the ac
the solution of hydrate of potash on indigo thus :—

$$3\,\overbrace{C_{16}H_5NO_2}^{\text{Indigo blue.}}+KO,HO+H_2O_2=\overbrace{KO,C_{16}H_6NO_5}^{\text{Isatate of potash.}}+2\,\overbrace{C_{16}H_6NO}^{\text{White indig}}$$

By exposure of the solution of the yellow crystals to t
oxygen is absorbed and indigo blue is deposited. If ind
fused with hydrate of potash, hydrogen is evolved and s
acid is amongst the products; but if to a concentrated
solution of potash indigo be added, care being taken to
the water as it evaporates, and if to the boiling liquid po
peroxide of manganese be added until the solution ceases to
indigo when exposed to the air, a different compound is the
and anthranilic acid is obtained in combination with
Anthranilic acid ($HO,C_{14}H_6NO_3$) may be procured by neut
the potash with sulphuric acid, evaporating to dryness, dis
the anthranilate of potash by means of alcohol, which lea
sulphate, and decomposing the anthranilate of potash by the a

etic acid. On evaporating the alcoholic solution, this acid is ined in brilliant plates, or in four or six-sided needles. Anthra- is metameric with benzamic acid (1246). If heated gently it be sublimed unchanged, but if the temperature be suddenly d the acid becomes decomposed into aniline and carbonic d:—

$$\overbrace{HO,C_{14}H_6NO_3}^{\text{Anthranilic acid.}} = \overbrace{C_{12}H_7N}^{\text{Aniline.}} + C_2O_4.$$

(1328) *Isatin* ($C_{16}H_5NO_4=147$).—This substance, which con- s two equivalents more of oxygen than indigo blue, may be ined by heating indigo in a dilute solution of bichromate of sh and sulphuric acid, or by the following process:—Powdered mercial indigo, of good quality, is to be mixed with a sufficient ntity of water to reduce it to a thin cream, and the mixture is e heated till it boils: undiluted nitric acid must then be added mall quantities at a time until the blue colour has disappeared; parts of indigo require 6 or 7 parts of acid. The mass con- ning isatin mixed with a large quantity of a brown resinous tter must next be largely diluted with water, boiled, and filtered lst boiling hot; the undissolved residue must be again boiled h water, and the filtered solution added to the first portions: stals are deposited as the liquid cools; they must be washed h water containing a little ammonia, then dissolved in alcohol recrystallized. When considerable quantities of isatin are re- red, Hofmann purifies the crude product of the action of nitric upon indigo by dissolving it in a dilute solution of potash; rochloric acid is then added to the deep brown liquid until the ipitate, which is at first brown, assumes a clear red tint, the id is then filtered and precipitated by an excess of hydrochloric ; the precipitate consists of isatin, which, after washing with water, is chemically pure.

Isatin crystallizes in brilliant, transparent, orange-coloured six- d, or rhombic prisms; it is sparingly soluble in cold water, is more readily dissolved by boiling water, and still more so by alcohol. Ether dissolves it less readily. On the application eat to the crystals they melt and are volatilized, emitting acrid ours of a yellow colour. When isatin is distilled in closed els a considerable portion of it undergoes decomposition. Isa- is capable of exchanging an equivalent of hydrogen for one of etal; thus, if an alcoholic solution of isatin be mixed with one of ate of silver, a wine-red amorphous precipitate of *argentisatin* H_4AgNO_4) is formed. Solution of potash dissolves isatin freely, forms a purple *liquid, which on boiling* becomes yellow. When examined after this change of colour has occurred, the ele of the isatin are found to have combined with those of water, producing *isatic acid* ($HO,C_{16}H_6NO_5$), which remains in com tion with the potash.

If isatin be heated with solid hydrate of potash it is de posed, hydrogen is liberated, carbonic acid is formed and is re in combination with the potash, whilst aniline distils over:—

$$\overbrace{C_{16}H_5NO_4}^{\text{Isatin.}}+4\,(HO,KO)=\overbrace{C_{12}H_7N}^{\text{Aniline.}}+2\,(2\,KO,C_2O_4)+H$$

Concentrated nitric acid decomposes isatin; when heated it copious ruddy fumes are evolved, a brown resinous body taining peroxide of nitrogen is formed, and if the action be c further oxalic acid is found in the solution. No carbazotic formed. Chlorine, if transmitted through water in which is suspended, displaces one equivalent of hydrogen and chlorisatin.

(1329) The *action of chlorine upon indigo* is peculiar: g chlorine has no action upon dry indigo, but if a current of ch gas be transmitted through water containing indigo in suspe the blue colour is gradually destroyed, and a rusty brown com is formed: this substance, in addition to formic acid, muriate monia, and a brown resinous substance, contains four distinct rinated compounds. Two of these, viz., *chlorisatin* $C_{16}H_4ClNO$ *dichlorisatin* $C_{16}H_3Cl_2NO_4$, are yellow, sparingly soluble, crys able substances formed upon the type of isatin. A third chlor compound is *trichloraniline* ($C_{12}H_4Cl_3N$), and it is usually acc nied by a certain quantity of *trichlorophenic* acid ($HO,C_{12}H$ Chlorisatin and dichlorisatin are soluble in alcohol; when with a solution of potash they yield acids,—the *chlorisatic* $C_{16}H_5ClNO_5$), and *dichlorisatic acid* ($HO,C_{16}H_4Cl_2NO_5$), corre ing with isatic acid; and, if distilled with hydrate of potash, give chlorinated bases of a composition corresponding to t aniline,—

Chloraniline being composed of $C_{12}H_6ClN$, and
Dichloraniline of . . . . . $C_{12}H_5Cl_2N$.

The reaction is precisely analogous to that with pure thus:—

$$C_{16}H_4ClNO_4+4\,(KO,HO)=C_{12}H_6ClN+2\,(2\,KO,C_2O_4)+H$$

The action of bromine upon indigo is analogous to th chlorine, though it is less violent.

(1330) *Ammoniacal derivatives of Isatin.*—When isat treated with ammonia it gives rise to a number of amidated

s, the composition of which varies with the degree of concen-
on of the ammonia : they have been particularly studied by
rent (*Ann. de Chimie,* III. iii. 483). The following table
bits the reactions which attend their formation :—

esatin . . . . $C_{16}H_6N_2O_2 = \overbrace{C_{16}H_5NO_4}^{\text{Isatin.}} + H_3N - H_2O_2$
asatin . . . . . . $C_{32}H_{11}N_3O_6 = 2\ C_{16}H_5NO_4 + H_3N - H_2O_2$
mic acid . . . . $HO,C_{32}H_{12}N_3O_7 = 2\ C_{16}H_5NO_4 + H_3N$
asatin or isamide . . $C_{32}H_{14}N_4O_6 = 2\ C_{16}H_5NO_4 + 2\ H_3N - H_2O_2$
timide . . . . . . $C_{48}H_{17}N_5O_8 = 3\ C_{16}H_5NO_4 + 2\ H_3N - 2\ H_2O_2$

risatin and dichlorisatin when heated with ammonia yield
sponding compounds.

(1331) *Isathyd* ($C_{16}H_6NO_4$).—This substance stands in the
relation to isatin that white indigo does to blue indigo ; that
say, it contains one equivalent more of hydrogen than isatin.
rder to procure isathyd, an alcoholic solution of isatin is mixed
one of hydrosulphate of ammonia, and set aside for a week in
sed bottle ; crystals of sulphur are gradually deposited, mixed
prismatic needles of isathyd. The sulphur must be removed
digestion with bisulphide of carbon. A better method, how-
, consists in placing powdered isatin in a flask with a consider-
quantity of water acidulated with sulphuric acid, then intro-
g a plate of pure zinc, and heating the whole to the boiling
t. As the isatin becomes dissolved, it combines with the
nt hydrogen, and is converted into isathyd, which is deposited
he form of a crystalline powder. Isathyd is a greyish white,
less substance, which is insoluble in water, and but sparingly
ble in alcohol and in ether even at a boiling temperature : it
eposited from these solutions as they cool in minute oblique
ms. If heated, it softens and becomes decomposed, and
uires a violet-brown tint. Boiling nitric acid colours it violet,
d dissolves it. Chlorisatin and dichlorisatin, when treated with
rosulphate of ammonia, yield chlorinated bodies corresponding
h isathyd, termed *chlorisathyd*, $C_{16}H_5ClNO_4$, and *dichlorisathyd*,
$H_4Cl_2NO_4$. By analogous methods corresponding compounds
taining bromine may be obtained.

When a current of sulphuretted hydrogen is transmitted
ough a boiling concentrated alcoholic solution of isatin, the
tin is converted into isathyd, and this, at the moment of its
mation, becomes decomposed, and *disulphisathyd*, a sulphuretted
pound corresponding in composition to isathyd, but containing
ivalents of sulphur in place of two equivalents of oxygen, is
d :—

$$2\,\overbrace{C_{16}H_5NO_4}^{\text{Isatin.}}+H_2S_2=2\,\overbrace{C_{16}H_6NO_4}^{\text{Isathyd.}}+S_2\text{; and}$$

$$\overbrace{C_{16}H_6NO_4}^{\text{Isathyd.}}+H_2S_2=\overbrace{C_{16}H_6NO_2S_2}^{\text{Disulphisathyd.}}+H_2O_2.$$

When the liquid has become clear by the deposition of the sulphur, the disulphisathyd may be precipitated by the addition of water: It is a yellowish grey, tasteless powder, which softens at 212°; alcohol and ether dissolve it, but do not yield it in a crystalline form on evaporation.

Various other sulphuretted derivatives may be obtained from isatin (Laurent, *loc. cit.*)

(1332) *Indin* ($C_{32}H_{10}N_2O_4$).—This substance appears to be polymeric with indigo blue. It is of a beautiful rose-colour, is insoluble in water, and but sparingly soluble in alcohol and in ether, even at a boiling temperature. In order to prepare indin, disulphisathyd is triturated in a mortar for some minutes with a concentrated solution of potash, adding a few drops of the alkaline solution from time to time, until a rose-colour begins to show itself. Alcohol is then to be added in small quantities at a time, continuing to triturate the mass until the mixture has assumed a deep rose-colour. It is then to be diluted with alcohol, and the insoluble portion collected on a filter and washed, first with alcohol, then with water. If this residue be dissolved in a tepid concentrated solution of potash, black needles of *indinate of potash* ($C_{32}H_9KN_2O_4$) are deposited. They must be washed with absolute alcohol, and decomposed with a weak solution of hydrochloric acid. Pure pulverulent indin is left on washing the insoluble residue. *Nitrindin* $C_{32}H_8(NO_4)_2N_2O_4$, *chlorindin* ($C_{32}H_8Cl_2N_2O_4$), and *dichlorindin* ($C_{32}H_6Cl_4N_2O_4$) are substitution compounds obtainable from indin.

Hydrindin ($C_{32}H_{11}N_2O_4+Aq$?)—This substance appears to stand in a similar relation to indin that reduced indigo does to blue indigo. When the black solution of indinate of potash is heated with an excess of an alcoholic solution of the alkali, the colour gradually changes into a pale yellow, and on cooling deposits crystals of *hydrindinate of potash.* Water decomposes them, and leaves hydrindin in the form of a white powder, insoluble in water, and sparingly soluble in hot alcohol.

A number of other compounds have been obtained from indigo: they are described by Laurent, *Ann. de Chimie*, III. iii. 483, and by Erdmann (*Journ. für prakt. Chemie*, vols. xix., xxii., and xxiv.)

(1333) 2. COLOURING MATTERS OF THE LICHENS.—Many of ichens afford colouring matters which are of considerable imance. A yellow lichen common on old walls (*Parmelia pariecontains* a colouring matter identical with that of the rhubarb (1311), and the different varieties of *Usnea* and *Evernia* ish an analogous, straw yellow, crystalline substance, termed *acid* ($HO,C_{38}H_{15}O_{13}$?), which is easily dissolved by ether; elds red compounds with the alkalies. When boiled with an of alkali it furnishes a substance termed by Stenhouse *beta-* ($C_{16}H_{10}O_4$?) The same compound is obtained by the distiln of usnic acid. These acids are unimportant as colouring ers and need not be further noticed here.

(1334) The red, violet, and blue colours, which are known in merce under the names of *archil*, *cudbear*, and *litmus*, are supby different species of *Roccella*, *Variolaria* and *Lecanora*. *Roccella* tribe grow upon rocks on the sea-coast, in the Canary nds, in Sardinia, and in Corsica, at the Cape of Good Hope, he western coast of South America, and in various other parts he world. The *Variolaria* abounds in certain parts of the enees, and of the Alps; and the *Lecanora tartarea* is abundant the Swedish mountains.

In no case do these lichens furnish the colouring matter ready ed; but they contain from seven to twelve per cent. of various urless acids, such as the *erythric* ($C_{32}H_{16}O_{16}$?), *evernic* $O,C_{34}H_{15}O_{13}$?), and *lecanoric* acids ($HO,C_{32}H_{13}O_{13}$?); these s under the influence of alkalies are readily decomposed into acids (which are characterized by the production of a violet ur with chloride of lime), and into a colourless neutral substance, ned *orcin* ($C_{14}H_8O_4$). Orcin is the true colour-producing body; er the influence of ammonia it absorbs oxygen, and is conted into *orcein* ($C_{14}H_7NO_6$), an azotised compound possessed of h tinctorial power.

In the preparation of *Cudbear* the lichens (chiefly *lecanora area*) are first freed as far as may be from earthy impurities, are made up into a paste with a solution of ammonia of sp. gr. ut 0·990; formerly stale urine to which a quantity of lime had n added, for the purpose of liberating its ammonia, was used; mixture is then exposed for some weeks to the air, moistening om time to time with fresh quantities of the ammoniacal liquid. is thus obtained of an offensive odour and of an intense ed colour; when dried and reduced to powder it constitutes *lbear* of commerce. The colouring-matter of this dye-stuff mainly of orcein. Cudbear is employed chiefly for woollen goods, *to which it imparts* a brilliant but not very permanent dye, of various shades of violet, lilac, and purple. *Archil* is prepared by digesting the lichens in a hot solution of ammonia, allowing it to stand for a few hours, and exposing the clear solution which is drawn off from the lichen in deep jars to the air for about 3 weeks; the solution when concentrated by evaporation forms the archil liquor of commerce.

(1335) *Litmus* is obtained principally from the *Roccella tinctoria*: it is prepared by a process similar to that used for archil, but it is moistened with a mixture of carbonate of ammonia and carbonate of potash,—the addition of the carbonate of potash (or of soda) being essential to the development of the blue colour. During its preparation the mass at first assumes a red colour, but it ultimately becomes of an intense blue. It is made up with chalk or plaster of Paris into small cakes for the market. A small portion only of the colouring matter of litmus is soluble in water and in alcohol, but it is nearly all soluble in alkaline liquids. The chemical composition of litmus still demands further investigation. Kane (*Phil. Trans.*, 1840), states that litmus contains several principles; one is a red semi-solid substance, which he terms *erythrolein*: it is soluble in ammonia with a purple colour: another is *erythrolitmin*, which forms crystalline grains of a dark red colour, soluble in alcohol, but not in ether; it becomes blue by the action of potash: neither of these substances contains nitrogen. But the principal constituent of litmus consists of a third body termed *azolitmin*, in which nitrogen is present; it is insoluble in alcohol and in ether, and sparingly soluble in water; it is amorphous, and of a brown red colour. Ammonia dissolves it and forms a blue solution, which gives blue and violet lakes when mixed with the salts of several of the metals.

(1336) *Assay of Lichens for Colouring Matter*.—The different lichens contain variable amounts of colour-producing ingredients; consequently their commercial value is liable to great variation. Stenhouse estimates the comparative value of different samples by means of a standard solution of chloride of lime. A given weight of the lichens in powder is digested with slaked lime and water in order to extract the colorific acid, and on adding chloride of lime to this liquid a red colour is produced, which disappears in a few minutes, leaving a brownish yellow tint; fresh quantities of the chloride are added so long as this red coloration is produced by it. Another method also suggested by the same chemist consists in adding an acid to the solution of the lichen acids in lime water, and collecting and weighing the precipitate of the lichen acids. The colour-producing acids may be extracted by the g method (Stenhouse) :—The pulverized lichens are mixed ter, and, after standing for an hour, a quantity of slaked dded, and the mixture is allowed to digest for some time; n placed in a linen filter supported in a tin vessel with a ed bottom, and the liquid is gradually displaced by the addition of water, the washing being continued so long ltrate yields the characteristic purple red colour with solu- hloride of lime. On the addition of hydrochloric acid to red solution, the lichen acids are precipitated in the form hite gelatinous deposit, from which the water may be by pressure. The acids may then be crystallized from cohol, but they must not be boiled with alcohol, otherwise id ethers would be formed, into the composition of which enter. This remarkable power of etherifying alcohol is g chemical peculiarity of the lichen acids.

formulæ which represent the composition of the numerous es of the lichens are at present variously represented by chemists. Those proposed by Gerhardt are founded pon the analyses of Schunck and of Stenhouse: they explain in a simple manner most of the metamorphoses he lichen acids undergo, and they agree with the actual f analysis very nearly as well as the empirical formulæ provisionally by Stenhouse and other chemists* who have examined these compounds:—

	Gerhardt.		
d	$C_{38}H_{16}O_{14}$	$C_{38}H_{17}O_{14}$	Stenhouse
acid	$C_{32}H_{16}O_{16}$	$HO,C_{20}H_{10}O_{9}$	Do.
thrin	$C_{30}H_{20}O_{16}$	$C_{34}H_{24}O_{20}$	Schunck
nannite . . .	$C_{14}H_{16}O_{12}+Aq$	$C_{11}H_{14}O_{11}$	Stenhouse
in	$C_{36}H_{16}O_{14}$	$C_{38}H_{17}O_{15}$	Do.
eid	$C_{34}H_{16}O_{14}$	$HO,C_{34}H_{15}O_{13}$	Do.
do.	$C_{18}H_{10}O_{8}$	$HO,C_{18}H_{9}\,O_{7}$	Do.
do.	$C_{32}H_{14}O_{14}$	$HO,C_{18}H_{8}\,O_{8}$	Schunck
sellesic do. . .	$C_{16}H_{8}\,O_{8}$	$HO,C_{16}H_{8}\,O_{7}$	Stenhouse
(lecanoric) ether	$C_{4}\,H_{5}\,O,C_{16}H_{7}O_{7}$	$C_{4}\,H_{5}\,O,C_{18}H_{8}O_{8}$	Schunck
cid	$C_{18}H_{6}\,O_{8}$	$HO,C_{21}H_{7}\,O_{9}+Aq$	Do.
ric acid . . .		$HO,C_{36}H_{17}O_{14}$	Stenhouse
. . . .	$C_{14}H_{8}\,O_{4}+2\,Aq$	$C_{16}H_{11}O_{7}$	Do.
n	$C_{16}H_{10}O_{4}$	$C_{38}H_{24}O_{10}$	Do.
. . . .	$C_{14}H_{7}NO_{6}$		

7) *Erythric Acid*, or *Erythrin* ($C_{32}H_{16}O_{16}$?).—This com- ppears to be present in most of the lichens which yield It is soluble in about 240 parts of boiling water, but is nsoluble in cold water; hot alcohol also dissolves it, and the acid in stellate groups of needles. It is likewise

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Schunck (*Liebig's Annal.*, xli. 157; liv. 257; lxi. 64); Rochleder (*Ib.* xlviii. 1); Stenhouse (*Phil. Trans.*, 1848, p. 63; 1849, p. 393).

soluble in ether. When heated in a tube it is decomposed, and orcin is sublimed. The alkalies dissolve it with facility. When boiled with baryta, a carbonate of this base is formed, and orcin is liberated :—

$$\overbrace{C_{32}H_{16}O_{16}}^{\text{Erythric acid.}} = 2\,C_2O_4 + 2\,\overbrace{C_{14}H_8O_4}^{\text{Orcin.}}.$$

By long boiling of the aqueous solution of erythric acid, water is assimilated, and it is decomposed with evolution of carbonic acid into *picro-erythrin* :—

$$\overbrace{C_{32}H_{16}O_{16}}^{\text{Erythric acid.}} + 2\,H_2O_2 = C_2O_4 + \overbrace{C_{30}H_{20}O_{16}}^{\text{Picro-erythrin.}}.$$

Picro-erythrin ($C_{30}H_{20}O_{16}$?) is a colourless substance which is sparingly soluble in cold water, but very soluble in boiling water, from which, on evaporation, it may be obtained in confused crystals. It has a very bitter taste. Its solutions give a precipitate with subacetate of lead, but none with the neutral acetate : with perchloride of iron it produces a beautiful purple colour. If heated alone in a tube it yields a sublimate of orcin. Alkalies dissolve it readily without the aid of heat. Its ammoniacal solution quickly becomes red by exposure to the air. When boiled with milk of lime or with baryta water it is decomposed, carbonate of lime or of baryta is formed, and orcin and a new body termed *erythro-mannite* are produced :—

$$\overbrace{C_{30}H_{20}O_{16}}^{\text{Picro-erythrin.}} + 2\,H_2O_2 = C_2O_4 + \overbrace{C_{14}H_8O_4}^{\text{Orcin.}} + \overbrace{C_{14}H_{16}O_{12}}^{\text{Erythro-mannite.}}.$$

Erythro-mannite, Pseudo-orcin, or *Erythro-glucin* ($C_{14}H_{16}O_{12}$ + Aq ; Gerhardt ; *Sp. gr.* 1·59 ; *Fusing pt.* 248°), is probably homologous with mannite. It may be extracted from the solution of the *roccella* in lime water, by boiling it for some hours in an open capsule, and then removing the excess of lime by means of a current of carbonic acid. On evaporation a syrupy mass is obtained, consisting chiefly of orcin and erythro-mannite ; the former may be extracted by means of ether or of alcohol. Erythro-mannite crystallizes from the residue in the course of a few days, and may be purified by washing it with cold alcohol and recrystallizing from boiling alcohol. Its aqueous solution deposits it in broad voluminous, brilliant crystals, belonging to the pyramidal system. When heated it undergoes fusion at 248°, but it may be heated to 480° without further change. Erythro-mannite is neutral to test papers ; it is very soluble in water, and has a sweet taste, but it is not fermentable. When heated with stearic or benzoic acid in sealed tubes to between 390° and 480° combination occurs with elimination of water; tartaric acid has a similar effect at 212°. When treated with fuming nitric acid kept cool, it yields an explosive compound, $C_{14}H_{10}(NO_4)_6O_{12}$, which corresponds to nitro-mannite (956): this body may be crystallized from its solution in boiling alcohol in brilliant laminæ, fusible at 142°. By prolonged treatment with nitric acid erythro-mannite yields oxalic, but no mucic acid. Its solution does not reduce the tartrate of copper and potash, nor does it yield any precipitate with ammoniacal acetate of lead.

(1338) *Evernic Acid* ($HO,C_{34}H_{15}O_{13}$?) occurs associated with usnic acid in the *Evernia prunastri*. It is scarcely soluble in water, even when at a temperature of 212°, but is readily soluble in alcohol and in ether; with potash and baryta it yields soluble crystallizable salts. When boiled with lime or baryta in excess, orcin is formed, and a new acid termed *evernesic acid*:—

$$\overbrace{C_{34}H_{16}O_{14}}^{\text{Evernic acid.}}+H_2O_2=C_2O_4+\overbrace{C_{18}H_{10}O_8}^{\text{Evernesic acid.}}+\overbrace{C_{14}H_8O_4}^{\text{Orcin.}}.$$

Evernesic acid does not yield orcin; ammonia does not produce any red colour with it; nor does chloride of lime yield with it a red or violet colour.

(1339) If the *Lecanora tartarea* and some other lichens be treated with ether, and the solution be evaporated, white crystals of *lecanoric acid*[*] ($C_{32}H_{14}O_{14}$?) are deposited; this substance is nearly insoluble in cold water, but it is freely dissolved by hot alcohol and by ether; its solution reddens litmus. Perchloride of iron strikes a dull purple red with its spirituous solution. If boiled with alcohol it produces a true compound ether. The caustic alkalies dissolve lecanoric acid, and deprive it of carbonic acid, leaving *orcin* in solution. Orcin is also obtained by simply heating lecanoric acid and distilling. If lecanoric acid be treated with ammonia and exposed to the air, the acid combines with the elements of ammonia, and a purple colour is gradually developed, owing to the production of orcein.

Alpha-orsellesic Acid ($HO,C_{16}H_7O_7$) is one of the products of the decomposition of lecanoric acid when its solution is boiled for a short time with an excess of lime or of baryta; by prolonged boiling it becomes converted into orcin:—

$$\overbrace{C_{32}H_{14}O_{14}}^{\text{Lecanoric acid.}}+H_2O_2=\overbrace{2\ C_{16}H_8O_8}^{\alpha\text{ Orsellesic acid.}};\ \text{and}$$

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[*] Lecanoric acid, according to Gerhardt, is identical with the alpha and beta orsellic acids of *Stenhouse*.

$$\overbrace{C_{16}H_8O_8}^{\alpha\text{ Orsellesic acid.}} = C_2O_4 + \overbrace{C_{14}H_8O_4}^{\text{Orcin.}}.$$

When either lecanoric or erythric acid is boiled with alcohol for some hours, orcin is separated, and a substance termed *pseudo-erythrin* or *lecanoric ether*, more properly *orsellesic ether* (C_4H_5O, $C_{16}H_7O_7$), is formed: it crystallizes in plates or needles, which may be purified by recrystallization from boiling water. It is scarcely dissolved by cold water, but is very soluble in alcohol and in ether, as well as in alkaline solutions, from which it is precipitated unaltered on the addition of an acid. Its ammoniacal solution, when exposed to the air, assumes a wine-red tint.

In certain cases Schunck found an acid which he terms *parellic acid* ($HO,C_{21}H_7O_9 + Aq$?), accompanying lecanoric acid; it is a fusible compound, which does not yield orcin when treated with alkalies. It crystallizes in brilliant, colourless, heavy needles, which are very sparingly soluble in cold water, but freely soluble in ether and in alcohol. The alcoholic solution has a very bitter taste; water precipitates the acid from it in a gelatinous form. It forms a white insoluble salt with baryta.

(1340) *Orcin* ($C_{14}H_8O_4 + 2\ Aq$; Gerhardt), *Sp. gr. of vapour* 5·7, corresponding to 3 volumes.—This substance appears to exist ready formed in several lichens, but it is generally procured by decomposing evernic, erythric, or lecanoric acid, by boiling it with an alkali. Stenhouse prepares orcin by boiling the solution obtained by treating one of the varieties of the *roccella* or *lecanora* with lime for some hours, and concentrating it by evaporation. The excess of lime must then be removed by means of a current of carbonic acid, and the filtered liquid evaporated to the consistence of a syrup; this residue must be treated with boiling alcohol, and allowed to crystallize; the red crystals of orcin thus obtained must be purified by recrystallization from their solution in ether. Orcin is a substance with a sweet but mawkish taste. It crystallizes with 2 Aq in colourless, quadrangular prisms, and is readily soluble in alcohol, ether, and water. When heated to 212° it melts and gives off its water of crystallization, and at 550° it may be sublimed unchanged. It is not susceptible of the vinous fermentation. In its anhydrous form it is metameric with saligenin. With persalts of iron it gives a dark red precipitate; it gives no precipitate with neutral acetate of lead, but with subacetate of lead a white precipitate is occasioned ($C_{14}H_6Pb_2O_4,2\ PbO$). With chloride of lime orcin gives a purple red colour, which quickly changes to a deep yellow. Nitric acid converts orcin into oxalic acid, and a resinous substance. If orcin be heated with stearic acid to 482° the two bodies unite, forming a waxlike body, analogous to the compound of mannite with the fatty acids.

Orcein ($C_{14}H_7NO_6$).—If orcin be exposed in a shallow dish under a bell-glass with air to the vapour of ammonia, it yields a fine red colour; oxygen is absorbed, and a compound is obtained which has received the name of *orcein* :—

$$2\,\overbrace{C_{14}H_8O_4}^{\text{Orcin.}}+2\,H_3N+3\,O_4=2\,\overbrace{C_{14}H_7NO_6}^{\text{Orcein.}}+4\,H_2O_2.$$

The aqueous solution of the result of the foregoing reaction contains orceinate of ammonia, and must be mixed with acetic acid, when orcein falls in red flocculi. Orcein is sparingly soluble in water, from which it is completely precipitated on the addition of a neutral salt. Alcohol dissolves it freely, forming a scarlet solution. It is sparingly soluble in ether. Potash and ammonia dissolve it readily, forming a splendid purple colour, which is the basis of the ordinary archil of commerce; the addition of common salt precipitates it from its solutions in the alkalies. With metallic salts its alkaline solutions yield beautiful purple lakes. The addition of acids restores its red tint, hence its value in the form of litmus as a test for free acids. If a solution of orcein be treated with hydrochloric acid and zinc in closed vessels it becomes colourless, but it resumes its red colour on exposure to the air.

Beta-Orcin ($C_{16}H_{10}O_4$?), the compound obtained by distillation of usnic acid (1333), is regarded by Gerhardt as a homologue of orcin: it is easily soluble in boiling water, alcohol, and ether; it has a slightly sweet taste. When mixed with ammonia it rapidly acquires a fine red tint. With caustic potash it yields a fine purple, and by chloride of lime its colour is instantly converted into a blood-red.

(1341) The vegetable colours are not the only ones which are used in dyeing; a beautiful blue is now prepared from ferrocyanide of potassium and the persalts of iron. A yellow is produced by chromate of lead, and an orange upon woollen and silken goods by means of concentrated nitric acid.

A variety of colours are used by the artist as pigments; most of these are obtained from the mineral kingdom: many of these mineral colours are wanting in transparency and brilliancy, but they are generally very durable. The pigments procured from the vegetable kingdom are more brilliant but less permanent, and in the small number of cases in which colours are obtained from the animal creation they generally combine durability with brilliancy. Several of the pigments in common use, such as the preparations of lead, arsenic, and copper, are poisonous. Many of the metallic colours, particularly those which contain lead, are injured by exposure to sulphuretted hydrogen, and become black. Vegetable colours are especially prone to fade under the influence of atmospheric oxygen, aided by a strong light.

(1342) *Colouring Matters of Plants and of Flowers.*—*Chlorophyll*, as the green colouring matter so generally diffused through the vegetable kingdom is termed, appears to be of a resinous nature. It is soluble in alcohol and in ether, but insoluble in water. The alcoholic solution is of a beautiful green colour, and on evaporation leaves the chlorophyll in an amorphous state. If the leaves be treated with ether, the colouring matter is dissolved, but it is accompanied by a wax-like body, which is insoluble in cold alcohol. When present in the leaf it undergoes various changes of colour, according to the plant in which it occurs. In autumn, before the leaves fall, it generally passes into yellow, as may be seen in the lime, the poplar, the horse-chestnut, and the common laurel. In other cases the colour changes to red of various shades, as in the Virginia creeper, the Spanish chestnut, and the sumach. Chlorophyll, according to Fremy, consists of a blue colouring principle, *phyllocyanin*, and a yellow one, *phylloxanthin*, and he attributes the yellow colour acquired by the fading leaves of autumn to the gradual destruction of the blue constituent. He found this yellow colouring matter to become green under the action of hydrochloric acid. Phylloxanthin was found by Kromayer as a fusible yellow body of butyraceous consistence, soluble in ether, alcohol, and bisulphide of carbon. Phyllocyanin is an azotised body ($C_{34}H_{34}N_2O_{17}$?) of a dark blue colour, soluble in cold alcohol but insoluble in water. Kromayer separated the two bodies by dissolving chlorophyll in alcohol and boiling the solution for a few minutes with an alcoholic solution of potash; then, on neutralizing with hydrochloric acid, a yellow precipitate was obtained, leaving the supernatant liquid of a beautiful blue. On evaporation, this blue liquid deposited blue flocculi insoluble in water.

Fremy and Cloez have examined the colouring matters of various flowers, and they consider that these tints may be referred to three distinct substances, one of which is of a blue or rose colour, while the other two are yellow. The blue or rose colour is produced by a compound which has been termed *cyanine*, the blue tint becoming red when exposed to the action of an acid. Red flowers have been observed to possess a juice the reaction of which is acid, whilst in blue flowers the juice is neutral. Cyanine may be obtained from the petals of the violet, or of the iris. *Xanthine* is the name given to the yellow matter which is insoluble in water: the petals of the sunflower contain xanthine in abundance. The yellow substance which is soluble in water is termed *xantheine*: it becomes brown by the action of alkalies, and may be obtained from the yellow dahlia. Not one of these bodies, however, has been isolated in a pure condition, and there is considerable doubt whether the colours of the flowers of different plants be due uniformly to the same materials. The yellow colouring matters, however, are clearly of a nature different from that of the blues and reds. Many red flowers become blue and green as they wither, but they never become yellow. Blue flowers are also sometimes observed to fade into red before the colour disappears, but they never become yellow; and on the other hand, a yellow flower as it withers never becomes blue.

Dyeing and Calico Printing.

(1343) *Use of Mordants.*—Of the various colouring matters used in dyeing, some, like indigo and safflower, are capable of being permanently attached to the fabric, and of fully communicating their colour to it without the intervention of any other substance, and have hence been termed *substantive* colours; but the greater number of the colouring matters which are employed in the arts are removable by washing. Such is the case when calico, for example, is boiled in the madder vat, or when flannel is heated with infusion of cochineal. Hence it becomes necessary, in order to fix the colour upon the cloth, to employ various substances which possess a strong tendency to attach themselves to the fibres of the texture, and to combine chemically with the dye-stuff; they thus form the connecting link between the two. Bodies employed for this purpose are called *mordants*, and the colours which require such treatment are termed *adjective* colours. Various mordants are in use, some being better adapted to one dye, some to another. *Alumina*, in the shape of a mixture of alum and cream of tartar, is extensively employed for woollen goods and for silks; for calicoes acetate of alumina (1109), diluted till the solution has the sp. gr. 1·08, is much employed, especially for madder dyeing. It communicates to cloth impregnated with it a brown tint in the madder vat, if concentrated, and a red or pink if more dilute.

Peroxide of Iron is another mordant largely used; it is

through the vegetable [illegible] it gives
resinous nature. [illegible] mordant,
soluble in water, [illegible] valuable
colour, and on [illegible] both being
state. If the [illegible] of chromi
is dissolved, [illegible] as mordants
insoluble in [illegible]—The process of
various [illegible] goods
occurs. [illegible] of which is
into yellow [illegible], the cloth
chestnut, [illegible] it upon a
to red [illegible] cloth is thus
[illegible] bath, and a
[illegible]. In woollen
use, [illegible] the yarn previous
by the [illegible] the colouring
[illegible] subjected to the
[illegible] this method of
[illegible] piece.

[illegible] outline of the
[illegible] the account given
[illegible] complicated, and
[illegible] a good dye :—
[illegible] remove the weaver's

operation of *galling*. Every 100lb. of
bath containing twenty-five gallons of
, and 16½lb. of sumach. Having been
dergoes the process of mordanting; for
of alum, of sp. gr. 1·04, to which an
f soda has been added, is employed, and
is steeped for twelve hours, at a tempera-
dried and washed. The true process of
med in the madder vat, the proportion of
100lb. to 300lb. for every 100lb. of cloth.
is added to the vat, and a certain proportion
employed to clarify the liquid. The next
ring, or boiling the dyed goods with a weak
soda, with the view of discharging the brown
afterwards boiled under pressure, with a solution
of tin, in order to brighten the colour; and
oroughly rinsed, and dried by exposure on the

co *Printing.*—It is not necessary in woven goods
cloth should receive the mordant: if the latter be
aste with British gum, it may be applied to the
rns, by means of suitable machinery. If cloth thus
being allowed to dry, be passed through the dye-
ards well washed, the mordanted portions alone will
our. This kind of pattern dyeing is principally
cotton goods, and constitutes a very extensive branch
der the title of calico printing.
mordant with different dyes produces different tints.
ed with alum in a madder bath gives a red; but if
bath containing logwood, it is dyed black.
mordants produce different tints from the same
rial; for example, in a madder bath, a piece of calico
h iron gives a fine purple; but if it be mordanted
yields a pink or red colour; and a mixed mordant,
ron and alum, in suitable proportions, gives a cho-
colouring material employed in the bath consist of
oth mordanted with alum will be dyed yellow; if
h acetate of iron, it will acquire a dark drab, and
nt of alum and of iron will produce an olive.
producible are susceptible of almost infinite varia-
to the method adopted. The cloth, for example,
rely dyed first, and the colour may afterwards be
atterns. *Thus, if a pattern be printed upon the dyed*

cloth with tartaric acid thickened with gum, and dried, on passing it through a warm solution of chloride of lime the chlorine will be disengaged upon the spots to which the acid was applied, and the colour will be removed at these parts of the cloth only. If the pattern discharged be required to be dyed again, the acid may be mixed with some suitable mordant—suppose it be acetate of lead; and after washing out the solution of the chloride of lime, the cloth may be passed through another liquid, such as bichromate of potash; in this case a yellow pattern, due to the formation of chromate of lead, would be produced. In some cases it is found to be more convenient to mordant the whole cloth in the first instance, and afterwards to discharge the mordant in patterns. Thus a piece of calico which has been mordanted by means of a mixture of alum and iron mordants may be discharged in patterns: by putting citric acid upon it, the mordant will be discharged upon those spots only; if it be then well washed and immersed in a logwood bath, it will come out dyed of a brown colour in every part except the places to which the citric acid was applied.

Occasionally with substantive colours, such as indigo, what are called *resist-pastes* are used: if, for instance, patterns be printed upon the cloth, with nitrate of copper properly thickened, and the goods thus prepared be passed through the indigo vat, the nitrate of copper will act by oxidizing the indigo in the parts to which the salt is applied, and the dye-stuff will not soak into the cloth in its reduced form at those points: hence, the colouring matter may be readily washed away from the spots to which the resist-paste was applied, whilst it remains fixed firmly everywhere else.

A peculiar modification of the mode of fixing the colours has received the name of *steam colour-printing*. For steam colours peroxide of tin is generally employed as the mordant. The perchloride of tin is decomposed by an excess of potash, which dissolves the precipitated oxide, and into this solution, when properly diluted, the cloth is dipped, and allowed to dry. After this it is immersed in very dilute sulphuric acid, to neutralize the potash, whilst the peroxide of tin remains attached to the fibre: the colours, properly thickened, are then printed on in patterns, and the whole exposed to the action of steam. At this temperature the colour combines completely with the mordant, producing a brilliant effect.

CHAPTER IX.

PRODUCTS OF DESTRUCTIVE DISTILLATION.

5) (*a*) *Products of the Distillation of Wood and of Resins.*— tances which are formed during the destructive distilla- ood in closed vessels are very numerous. They vary with e of the wood operated on, and the temperature at which lation is effected. The decomposition commences slowly erature of about 280°. The volatile portion of the pro- udes substances which are gaseous, as well as those which or solid, whilst a considerable residue is left in the form al in the retort. Amongst the gaseous products of the n, the most abundant are carbonic acid, carbonic oxide, ogen. Of the liquid products one portion is soluble in e other portion is insoluble, and is of an oily consistence. le portion consists of acetic acid, wood spirit, acetate of nd acetone, accompanied by water, and by other bodies fectly known. The insoluble portion, which constitutes , is composed of a mixture of various liquids holding ters in solution, or in suspension: its most important ts are several forms of hydrocarbon, such as toluol, nol, and other bodies, such as eupion, which have been ctly examined, besides a number of oxidized compounds, kreasote, picamar, and kapnomor. Amongst the solid are resinous matters more or less resembling colophony, xy body, which has been termed paraffin; there are also er bodies, such as naphthalin, cedriret, pittacal, pyrene, , and pyroxanthin.

products of the distillation of wood obtained at the lowest ure are those into the composition of which oxygen enters tly, such, for example, as water, acetic and carbonic acids. emperature rises, compounds containing less oxygen are formed, such as wood spirit, acetone, and kreasote; at a re elevated temperature various hydrocarbons, such as ylol, eupion, and the different forms of paraffin are pro- hilst as the temperature approaches to redness, pure predominates.

e distillation in iron cylinders of air dried hard woods, ak or beech, the charcoal reaches about 25 per cent. of the the wood employed, or about three-fifths of the quantity present in the wood. The liquid portion, amounting to about 53 per cent., containing about one-fifth of the entir tity of carbon in the wood; and the remaining portion distillate, consisting of uncondensed gases, carries off the re of the carbon. Among the liquid products acetic acid amo between 3 and 4 per cent. of the weight of the harder naphtha to about 1 per cent., and the tar to 7·5 per cent.

Stockholm tar, so largely used in ship-building, is obtai a rude kind of distillation of the resinous wood of the pi conical cavity is formed in the side of a hillock, the apex cone being below, and terminating in an aperture that ope a trough leading to a reservoir for the tar. The kiln is with wood, and covered over incompletely with turf; the lighted at the top, and the combustion regulated by cov in more or less completely; the wood is thus charred from downwards, and the tar flows off at the bottom, charged considerable quantity of resin, and mixed with acetic acid of turpentine. When heated, an impure essence of turpe distilled, leaving a black resinous substance, which cons ordinary *pitch*. The specific gravity of the ordinary tar o merce is about 1·040.

In preparing pyroligneous acid, wood which contai little resin is used, and the condensation is more complete. tar is of a different kind, and contains a variety of products, have been already enumerated.

(1347) *Paraffin* (xCH) *Sp. gr.* 0·870.—This name wa given by Reichenbach to a crystalline substance found a the solid constituents of tar. It comes over during t stages of the distillation, when the crude tar is rectified. P is particularly abundant in beech tar, but according to Re bach it is also found in the tar of both animal and vegetab stances, as well as in that of pitcoal. At ordinary temper beechwood paraffin is a hard crystalline white substance, either taste or odour, somewhat brittle, and resembling sper both to the touch and in appearance. It fuses at 110·7 colourless oily liquid, which remains transparent after sol tion, and at a higher heat may be distilled unchanged. I not dissolve camphor, naphthalin, or pitch when fused with but may readily be mixed with stearin, spermaceti, bees wa common resin. Cold olive oil dissolves it sparingly till with it, but hot oil dissolves it freely. Oil of turpentin benzol dissolve it abundantly; so also does ether. Boiling lute alcohol does not take up more than 3·45 per cent. weight, and deposits the greater part on cooling in cryst plates. Paraffin is insoluble in water. It burns with a

less flame; candles made of it burn like those made of the
wax. The strongest acids and alkalies, and even chlorine,
at a high temperature, are without effect upon it; hence it
ceived the name of *paraffin* (from *parum affinis*). In order
ate the paraffin, the heaviest portion of the tar oils is gra-
mixed with from ¼ to ½ its weight of oil of vitriol. The
ature rises rapidly, and a black liquid is formed, which
ulphurous acid. The temperature must be raised to 212°,
s not reach that point spontaneously; the mixture must then
ntained at rest in a place the temperature of which is not
to fall below 120°. A colourless liquid rises to the surface;
be allowed to cool, when it will become solid. If now it
ed and submitted to pressure, a liquid oil will be removed
paraffin may be purified by crystallization from alcohol.
dies termed *cerene* and *melene*, which Brodie obtained
the distillation of wax (1055), are very similar to this sub-
and contain carbon and hydrogen in equal atomic propor-
It is probable that many substances termed paraffin consist
ixture of several polymeric hydrocarbons, which form the
terms of the series to which olefiant gas belongs; the
point of different bodies presenting the appearance and
es of paraffin varying between 110° and 149°. It is,
r, very difficult to determine by analysis of the higher
of the series, whether their formula should be $C_{2n}H_{2n}$ or
$_{+2})$, which latter view Anderson is inclined to support.
is an abundant constituent of Rangoon petroleum, and
ise obtained in considerable quantity from the products of
illation of peat, as well as of certain forms of lignite. But
n supply of the solid paraffin of commerce is obtained from
illate of the bituminiferous substance known as *Boghead*
(note, p. 125).

raffin Oil.—Amongst the products of the distillation of Bog-
annel is a large quantity of an oily matter, the proportion of
greater, the lower the temperature at which the distillation
ted. The oil is almost entirely free from oxygen. When
, a volatile portion may be separated from it, which,
ng to G. Williams, contains several of the radicles of the
, including tetryl and amyl. The compounds which come
a higher temperature appear to belong to the hydrocarbons
rm of $(C_{2n}H_{2n})$, or possibly $(C_{2n}H_{2n+2})$. For practical pur-
hey may be separated into three portions, one of which
liquid at very low temperatures; the sp. gr. of this is
820, and *it boils at 418° or upwards*: it is largely used in
ource of light, under a variety of names. The second

portion, which is distilled at a higher temperature, depos
of a solid hydrocarbon (one of the forms of paraffin), when
a great reduction of temperature, and the last portic
distillate are semi-solid at ordinary temperatures. It i
therefore, that the products of the distillation of th
contain a mixture of several substances, the less volatil
are found by analysis to consist of hydrocarbons of the
as paraffin. The less volatile liquid portion of the oil s
paraffin in solution in a mixture of liquid hydrocarbons
the same ultimate composition as paraffin. This oil is
used under the name of *paraffin oil*, for the purpose of
machinery, to which use it is admirably adapted, since i
become oxidized or thickened by exposure to the air, an
rates but slowly.

(1348) *Pyrene and Chrysene.*—In the later stages
tillation of fatty and of resinous bodies, and in that of
yellow powder is sublimed, which contains two substan
by Laurent, pyrene and chrysene. *Pyrene* ($C_{30}H_{12}$),
from πῦρ, fire, to indicate its origin from the action
soluble in hot ether, and may be separated from chrysen
of this solvent, which at a low temperature deposits it
scopic rhomboidal plates. It is insoluble in water, an
tute of odour; it fuses at about 350°, and may be di
altered. *Chrysene* $(C_{12}H_4)_2$? is a crystalline subst
beautiful yellow colour, whence its name, from χρὺσι
It is inodorous, insoluble in water and alcohol, and only slig
in ether: boiling oil of turpentine dissolves it more readily
It fuses at about 450°, and is partially decomposed when

(1349) *Pyroxanthin* ($C_{21}H_9O_4$? Gregory).—This
was discovered by Scanlan amongst the products of th
potash upon crude wood-spirit. When crude wood-spi
fied with lime, a dark brown residue remains in the re
when treated with hydrochloric acid leaves a brown
matter, consisting of pyroxanthin and a resinous subs
this residue be boiled in alcohol it is in great measure
and as the liquid cools, crystals of pyroxanthin are deposi
yellow needles, hence its name,—from πῦρ, fire, ξανθ
It is insoluble in water and in alkaline solutions, but
hot alcohol, ether, and acetic acid. It fuses at 291°, a
sublimed in a current of air at 273°. If it be subli
closed tube it undergoes partial decomposition. It is
sulphuric acid with a deep bluish red colour, and in hydroc
with a fine purple, which soon passes into dark brown. Py

lidify in shallow iron
nvas: the solid
fied by a repetition
sulphuric acid, and

treatment with oil of
ployed for lubricating

contains wood spirit,
use of concentrating and
hitherto been too great to
this liquor.

llation of *Pit-coal.*

stillation of pit-coal are still
d; and they are invested with
ir intimate connexion with the

burned in the open air, the principal
re carbonic acid and water, with
and sulphurous acid, derived from
nd the pyrites contained in the coal;
in a finely-divided form escapes com-
the soot or visible smoke of a coal fire.
of the coal is effected in vessels from
he products are much more numerous and
mount of volatile matter is expelled, partly
ensible gases, and partly in the form of
reduced to the ordinary temperature of the
or solids; whilst a large proportion of the
remains behind in the retort, and forms a
of coke, known as *gas coke.*

gaseous products the most important are marsh
hydrogen, carbonic oxide, carbonic acid, sulphu-
and ammonia. The liquid portions contain water,
ils of hydrocarbon, such as benzol, toluol, and
nstitute the chief ingredients of the liquid termed
esides which there is a large quantity of a dark
known as *coal tar*, the nature of which will be
considered hereafter (1356).

as is *to be employed for the purpose* of illumi-
r *of a dwelling-house,* it is not sufficient to con-

separation of hydrocarbons is effected. Lastly, the must be digested upon chloride of calcium, and distilled It may be regarded as pure if its boiling point be constan and if it does not become brown when kept.*

Properties.—Kreasote, when pure, is a colourless oi of high refractive power. It is not easily inflamed, bu kindled it burns with a smoky flame. Its taste is burn its odour extremely pungent and peculiar; if swallowed i of more than a few drops it acts as a poison. Kre sparingly soluble in water, to which it communicates its odour and pungent taste. It is soluble freely in acet alcohol, and ether, as well as in benzol and bisulphide of It combines with potash, and forms a crystalline compou it; solution of ammonia also dissolves it. Kreasote prod immediate coagulation of albumen. It is the most antiseptic known. Meat that has been plunged into a containing 1 per cent. of kreasote gradually becomes dry a on exposure to the air, and acquires the flavour of smok but does not become putrid. A considerable portion of (from 1 to 1¼ per cent) is held in solution in the cru ligneous acid obtained during the destructive distillation of and on saturating this acid at 167° with effloresced sul soda, an oily matter which contains a large proportion of is separated. Crude pyroligneous acid, on account of the which it contains, is frequently employed for preserving ha salted provisions, to which it communicates the same flav they had been exposed to wood smoke.

Kreasote when largely diluted is sometimes given inte order to check obstinate vomiting. If applied in a conc form to the exposed pulp of a carious tooth, it frequently instant relief in cases of acute toothache. It is also a application, in a very diluted form, in some cases of fœtid and in many cutaneous affections. If applied to the sk concentrated state it produces a white spot, the skin disorganized, and peels off without any attendant inflam Kreasote dissolves many organic bodies, such as camph [illegible] and volatile oils, and many of the resins.

It is not improbable that kreasote may be a homolo [illegible] acid, and that its true formula may be $C_{16}H_{10}O_2$. [illegible] by a mixture of chlorate of pota hydrochloric acid, yields perchloroquinone or chloranile (1163). Kreasote, when treated in a similar manner, furnishes a resinous mass, which after digestion with cold alcohol, leaves a compound resembling chloranile in appearance and properties ($C_{26}H_6Cl_6O_6$? Gorup Besanez). This new body crystallizes in brilliant, golden yellow plates; it is insoluble in water, sparingly soluble in cold alcohol, and freely soluble in ether; it may be sublimed at about 360°. Gerhardt has shown that the more probable formula $C_{16}H_4Cl_4O_4$ corresponds equally well with the results of its analysis, and in that case the compound would be homologous with chloranile, and would contain 2 (C_2H_2) more than the latter body.

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* [illegible] potash the kreasote appears to undergo o [illegible] removed, whilst the quantity of ox [illegible]

(1352) *Kapnomor* ($C_{20}H_{11}O_2$? Voelckel; from καπνὸς, smoke, and μοῖρα, a part); *Sp. gr.* 0·995.—This is a colourless oil of peculiar odour, which boils at about 360°. It is insoluble in water and in a solution of potash, but it is partially soluble in an alkaline solution of kreasote. It is soluble in sulphuric acid with a purplish red colour, and forms with it a colligated acid. Nitric acid converts it into oxalic and carbazotic acids, and another crystallized body which has not been examined. Kapnomor is obtained by distilling the crude solution of kreasote in potash with water: it passes over with the vapour of water.

Reichenbach has described various other compounds from tar, under the names of *pittacal*, a solid compound of a deep blue colour; of *picamar*, an oily body of sp. gr. 1·10, which has a very bitter taste, and forms a crystalline compound with potash; and of *cedriret*, which crystallizes in orange-red needles from a solution of persulphate of iron, and is dissolved with a blue colour in oil of vitriol; the properties of all these bodies have, however, been but incompletely examined.

(*b*) *Distillation of Peat.*

(1353) The distillation of peat has of late years been attempted on a considerable scale, and the results obtained are of sufficient interest to justify a brief notice in this place.

Attempts to effect the distillation of peat in closed cylinders in the manner practised for wood and coal, have failed in an economical point of view. The peat charcoal thus obtained is too bulky and too brittle to be commonly used with advantage as a fuel, whilst the percentage of ash which it yields is often extremely large. Of late years, however, a process has been in operation at Athy, near Kildare, in which the distillation of peat has been carried on by the heat *evolved during* its own combustion. This

dips downwards, terminating at *e*, bene
the liquid contained in a long and wide pipe, *f*, called
which passes horizontally along the front of
This pipe is kept constantly half full of
moisture. By this means the opening into e
closed by a water valve, which permits a c
and renewed in any one or more retorts, withou
the operation of those which are still in action.
accumulates in the hydraulic main, flows over into t
In about four hours after charging the retort,
given off nearly all its gas, and a fresh charge of
required; but it is not an unusual practice to charg
at intervals of six hours, since the gas, thou
is increased in quantity, and the coke is impro
When a charge is to be drawn, the mouth
opened, and the coke raked into large iron boxes,
extinguished by pouring water over it. A fresh sup
introduced by means of a long scoop, so tha
the required quantity of coal is placed at once upo
the retort, which is at a bright red heat. The do
prepared with fresh luting upon its edges, is inst
and the distillation proceeded with. In large gas
are so arranged that a fresh set shall require
in order that the gas which is produced shall
uniform in quality.*

Having deposited in the hydraulic main most o
water, containing in solution a good deal of
sulphate of ammonia, the gas passes next throu

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* The gas first given off is the best, and also the largest
having had time to rise to the full temperature of th
exposed to heat for five hours, much of the gas
consists of hydrogen and carbonic oxide, the coa
red hot throughout. The following details will
bushels of cannel coal, or the usual charge
were carbonized at a full cherry-red heat, and
was as follows :—

	Cubic Feet.
In the first hour . .	345 . . . .
. . . .	203 . . . .
. . . . . .	118 . . . .
. . . . .	54 . . . .
. . . . . .	20

in all to 740 cubic feet; but it will be o
hour, as well as the specific gravity, conti
proceeded. This was due to the diminuti
hydrocarbons, and the increase in th

the *refrigerators* or *condensers*, *j j*, a series of serpentine or con- ted tubes; these are kept cool by the extent of surface which y expose to the air, and their temperature, when neces- , may be reduced still further, by allowing cold water from the ern, K, to flow over their exterior: here most of the remaining and aqueous vapour become separated. From the condenser gas passes to the lime *purifiers*, L L′, which consist of cast-iron els containing a number of horizontal perforated shelves, *m m*, ged one above another; upon these shelves dry slaked lime is d, to the depth of about five inches. The gas enters at the m of the purifiers, and rises on one side through each layer e in succession,* descending on the other side of the purifier makes its exit at *n*. In these purifiers the gas loses carbonic sulphuretted hydrogen, sulpho-cyanogen, cyanogen, and traces phthalin which are still suspended in it; finally, it is caused to in bubbles through dilute sulphuric acid, with the view of ing the last portions of ammonia; but this part of the appa- is not represented in the figure.

many works the process of washing with acid is superseded use of an apparatus termed a *scrubber*, consisting of a tower, erior of which is filled with small coke resting upon per- shelves; through this mass of porous material a constant of fresh water is maintained, and by this arrangement the ich enters at the bottom of the tower, is exposed to a large nt surface, and the ammonia is effectually removed. This , however, somewhat diminishes the illuminating power of by removing a portion of the vapour of some of the more ible hydrocarbons which are held in suspension.

ixture of hydrated oxide of iron and moistened sawdust xtensively substituted for slaked lime in the purifier (636); other substances are also occasionally employed with a effectually arresting the sulphuretted and ammoniacal im-

The gas, after it has been thus purified, is stored up for mense reservoirs or gasometers of metal, P, each consist- large bell of sheet iron, inverted in a brickwork tank, *q*, h water, in which the bell rises and falls. The bell is in es nearly counterpoised by weights attached to chains, ss over pulleys suitably supported, or as is now more so constructed as to rise and fall by the admission or the gas without the necessity for such counterpoises.

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times the lime is made into a thin cream by admixture with water is caused to *stream in bubbles through the* mixture, but generally, *employed in the form of a slightly* damp powder.

volatilized consist .chiefly of
manent gases which have been
s. As the temperature rises,
iacal salts comes over, and a
pon the surface of the water in
roceeds, water ceases to come
creases, its density continuing
y exceeds that of water. The
n 5 to 10 per cent. of the tar.
mpounds which rapidly absorb
to become brown on keeping,
on of oil of vitriol, by which
ed into a tenacious tarry mass
which it is no longer soluble.
again rectified constitutes *coal*
ation of the coal-tar, a yellow
as *dead oil*, is obtained, the
) per cent. of the quantity of
s of the operation, naphthalin
ie oil becomes semi-solid as it
etort solidifies on cooling, and
he preparation of asphalt, and
production of a coarse black
k from rust. If it be desired
much higher temperature is
undergoes decomposition, and
has the consistence of butter;
At a still more advanced
acquires a yellow colour, and
and as the temperature of the
apours produced become con-
nge-coloured powder which is
l, agglutinates into a viscous
fly of the chrysene and pyrene
tort after it has ceased to give
rous coke which is difficult of

is seldom submitted to further
rbolic) acid, aniline, quinoline,
isting chiefly of hydrocarbons,
and which hold a considerable
ı. Heavy coal naphtha or
tic qualities, and is employed

The pressure, which is not usually
column of water two or three inches
the pipes or *main*, *o o*, by which i
consumers.

In the foregoing process one of
tance is the due regulation of the te
tion. The retorts should be heat
they be insufficiently heated, the p
tity of the vapours of condensible
the gasometers and the distributing
and inconvenience: whilst if the t
the gas after its production be allow
with the highly heated surface of th
decomposition; a portion of its car
dense layer upon the interior of
chokes up, and at the same time th
is proportionately diminished by the

In addition to this inconvenien
to be formed in small quantity if th
too high a temperature, and no econo
by which this body can be removed.
impurity is burned, it gives rise to
quantity of sulphuric acid, which
furniture of the building, on the
slowly corrodes and otherwise injure

(1356) *Compounds present in Co*
sity from 1·120 to 1·150; the light
proportion of liquid oils. Of the su
some are basic, and some acid, but th
neutral or indifferent bodies.

The bases include ammonia, an
pyridine (1185 *et seq.*). Among th
small amount, but the most importa
acid of Runge. This chemist al
termed *rosolic* and *brunolic* acids,
nation.

The neutral substances contain
ing benzol, toluol, cumol, and cymo
constituents; whilst naphthalin, ant
are among those which are solid at

The distillation of coal-tar is co
as a separate branch of trade. T
large iron retorts upon quantities

The first portions that are volatilized consist chiefly of ia accompanied by some permanent gases which have been d by the liquid hydrocarbons. As the temperature rises, harged with various ammoniacal salts comes over, and a rown oil gradually collects upon the surface of the water in eiver. As the distillation proceeds, water ceases to come nd the quantity of this oil increases, its density continuing ment until its specific gravity exceeds that of water. The il amounts generally to from 5 to 10 per cent. of the tar. istillate may be freed from compounds which rapidly absorb a and cause the distilled oil to become brown on keeping, itation with a small proportion of oil of vitriol, by which oxidizable products are converted into a tenacious tarry mass r than the rest of the oil, in which it is no longer soluble. purified supernatant oil when again rectified constitutes *coal tha.* By continuing the distillation of the coal-tar, a yellow y fœtid oil, technically known as *dead oil,* is obtained, the nt of which seldom exceeds 30 per cent. of the quantity of mployed. In the latter stages of the operation, naphthalin undant in the distillate, and the oil becomes semi-solid as it . The black residue in the retort solidifies on cooling, and s *pitch,* which is employed in the preparation of asphalt, and colouring ingredient in the production of a coarse black sh, used for protecting iron-work from rust. If it be desired rry the distillation further, a much higher temperature is red, when the pitch in its turn undergoes decomposition, and s a product which, when cool, has the consistence of butter; nsists chiefly of anthracene. At a still more advanced of the process, the distillate acquires a yellow colour, and nes the appearance of a resin; and as the temperature of the approaches a red heat the vapours produced become con- d in the form of a bright orange-coloured powder which is from odour, and when pressed, agglutinates into a viscous This substance consists chiefly of the chrysene and pyrene urent. The residue in the retort after it has ceased to give latile matters, forms a hard porous coke which is difficult of ustion.

he heavy coal-oil, or dead oil, is seldom submitted to further cation. It contains phenic (carbolic) acid, aniline, quinoline, variety of other bodies, consisting chiefly of hydrocarbons, boil between 390° and 570°, and which hold a considerable ity of anthracene in solution. Heavy coal naphtha or oil *is remarkable for its antiseptic* qualities, and is employed

The pressure, which is not usually allowed to exceed that of a column of water two or three inches in height, drives the gas along the pipes or *main, o o,* by which it is distributed to the various consumers.

In the foregoing process one of the points of greatest importance is the due regulation of the temperature during the distillation. The retorts should be heated to a bright cherry-red. If they be insufficiently heated, the products contain a large quantity of the vapours of condensible hydrocarbons, which collect in the gasometers and the distributing pipes, and occasion much loss and inconvenience: whilst if the temperature be too high, or if the gas after its production be allowed to remain long in contact with the highly heated surface of the retort, it undergoes partial decomposition; a portion of its carbon is deposited and forms a dense layer upon the interior of the retort, which it gradually chokes up, and at the same time the illuminating power of the gas is proportionately diminished by the loss of this carbon.

In addition to this inconvenience, bisulphide of carbon is apt to be formed in small quantity if the distillation be conducted at too high a temperature, and no economical means are as yet known by which this body can be removed. When gas which contains this impurity is burned, it gives rise to the production of a minute quantity of sulphuric acid, which gradually accumulates on the furniture of the building, on the bindings of books, &c., and slowly corrodes and otherwise injures them.

(1356) *Compounds present in Coal-tar.*—Coal-tar varies in density from 1·120 to 1·150; the lightest tar containing the largest proportion of liquid oils. Of the substances contained in coal-tar some are basic, and some acid, but the principal portion consists of neutral or indifferent bodies.

The bases include ammonia, aniline, picoline, quinoline, and pyridine (1185 *et seq.*). Among the acids, the acetic is present in small amount, but the most important is phenic acid, the carbolic acid of Runge. This chemist also mentions two other acids, termed *rosolic* and *brunolic* acids, which require further examination.

The neutral substances contain several hydrocarbons, including benzol, toluol, cumol, and cymol, which are among the liquid constituents; whilst naphthalin, anthracene, chrysene, and pyrene are among those which are solid at ordinary temperatures.

The distillation of coal-tar is conducted on an extensive scale, as a separate branch of trade. The operation is performed in large iron retorts upon quantities of several hundred gallons at a time. The first portions that are volatilized consist chiefly of ammonia accompanied by some permanent gases which have been dissolved by the liquid hydrocarbons. As the temperature rises, water charged with various ammoniacal salts comes over, and a fœtid brown oil gradually collects upon the surface of the water in the receiver. As the distillation proceeds, water ceases to come over, and the quantity of this oil increases, its density continuing to augment until its specific gravity exceeds that of water. The light oil amounts generally to from 5 to 10 per cent. of the tar. This distillate may be freed from compounds which rapidly absorb oxygen and cause the distilled oil to become brown on keeping, by agitation with a small proportion of oil of vitriol, by which these oxidizable products are converted into a tenacious tarry mass denser than the rest of the oil, in which it is no longer soluble. The purified supernatant oil when again rectified constitutes *coal naphtha.* By continuing the distillation of the coal-tar, a yellow heavy fœtid oil, technically known as *dead oil,* is obtained, the amount of which seldom exceeds 30 per cent. of the quantity of tar employed. In the latter stages of the operation, naphthalin is abundant in the distillate, and the oil becomes semi-solid as it cools. The black residue in the retort solidifies on cooling, and forms *pitch,* which is employed in the preparation of asphalt, and as a colouring ingredient in the production of a coarse black varnish, used for protecting iron-work from rust. If it be desired to carry the distillation further, a much higher temperature is required, when the pitch in its turn undergoes decomposition, and yields a product which, when cool, has the consistence of butter; it consists chiefly of anthracene. At a still more advanced stage of the process, the distillate acquires a yellow colour, and assumes the appearance of a resin; and as the temperature of the retort approaches a red heat the vapours produced become condensed in the form of a bright orange-coloured powder which is free from odour, and when pressed, agglutinates into a viscous mass. This substance consists chiefly of the chrysene and pyrene of Laurent. The residue in the retort after it has ceased to give off volatile matters, forms a hard porous coke which is difficult of combustion.

The heavy coal-oil, or dead oil, is seldom submitted to further purification. It contains phenic (carbolic) acid, aniline, quinoline, and a variety of other bodies, consisting chiefly of hydrocarbons, which boil between 390° and 570°, and which hold a considerable quantity of anthracene in solution. Heavy coal naphtha or dead oil is remarkable for its antiseptic qualities, and is employed

for the preservation of timber for railway sleepers, &c.
consumed as a fuel in common lamps, but it is chi
burning into lampblack.

The light naphtha obtained in the foregoing pr
mitted to rectification, by which it is separated into a n
portion, and an additional quantity of the heavy oil.
to agitate the rectified portion with oil of vitriol, which t
a deep red colour, and removes a large portion of t
which communicate to the crude distillate its offe
The mixture on standing separates into two layers, th
which is the purified naphtha. When this liquid is
mitted to distillation, the oil which comes over is free
thalin, and does not become coloured by exposure
Coal naphtha thus purified and sold as 'highly rect
in specific gravity from about 0·860 to 0·900. It
mixture of oils, which boil below 392°, and may be sep
each other by distillation.

Mansfield (*Q. J. Chem. Soc.*, i. 252) has made a
mination of the constituents of this naphtha. In his
he employed the crude light oil, before it had been
oil of vitriol, and having freed it from basic and ac
agitating it successively with dilute sulphuric acid
solution of potash, he submitted it to a systematic pr
tionated distillation. He thus found that at least
liquids may be separated from light coal naphtha. T
are:—1. An oil of a peculiar alliaceous odour, the
of which lies between 140° and 158° F.; this oil
small quantity, and has not been perfectly examined
contains a mixture of alcohol radicles. 2. An oil w
176°, consisting of benzol, $C_{12}H_6$. 3. An oil which h
235°, and consists mainly of toluol, $C_{14}H_8$. 4. An oi
between 288° and 293°, presenting the characters of cu
And 5. An oil which possesses the odour and other
cymol, $C_{20}H_{14}$, boiling at from 338° to 342°. The
more abundant in those portions of coal naphtha whic
than water.

(1337) *Homologous Hydrocarbons from Coal T*
toluol, cumol, and cymol belong to the same homo
Xylol, the hydrocarbon intermediate between toluo
was found by Cahours among the products of the
wood.

It would be easy, in connexion with these hyd
form a table, of which the following is a fragment,

ne principle as that given at pp. 34 and 35. The com- of the various series of which it consists, with the excep- the derivatives of benzol, have been, however, only incom- examined :—

Homologous Derivatives of Coal-tar Hydrocarbons.

	Chloride.	Nitro-compound.	Dinitro-comp'd.	Amide-base.	Acid.
H	$C_{2n}H_{2n-7},Cl$	$C_{2n}H_{2n-7},NO_4$	$C_{2n}H_{2n-}N_{8}(O_4)_2$	$C_{2n}H_{2n-7},H_2N$	$HO,C_{2n}H_{2n-7},O$
H	Chlorobenzol. $\overbrace{C_{12}H_5,Cl}$	Nitro-benzol. $\overbrace{C_{12}H_5,NO_4}$	Dinitro-benzol. $\overbrace{C_{12}H_4(NO_4)_2}$	Phenylia. $\overbrace{C_{12}H_5,H_2N}$	Phenic acid. $\overbrace{HO,C_{12}H_5,O}$
H	Chlorotoluol. $\overbrace{C_{14}H_7,Cl}$	Nitro-toluol. $\overbrace{C_{14}H_7,NO_4}$	Dinitrotoluol. $\overbrace{C_{14}H_6(NO_4)_2}$	Toluylia. $\overbrace{C_{14}H_7,H_2N}$	Kresylic acid. $\overbrace{HO,C_{14}H_7,O}$
H		Nitro-xylol. $\overbrace{C_{16}H_9,NO_4}$		Xylylia. $\overbrace{C_{16}H_9,H_2N}$	Kreasote (?) $\overbrace{HO,C_{16}H_9,O}$
H		Nitro-cumol. $\overbrace{C_{18}H_{11},NO_4}$	Dinitrocumol. $\overbrace{C_{18}H_{10}(NO_4)_2}$	Cuminylia. $\overbrace{C_{18}H_{11},H_2N}$	
H		Nitro-cymol. $\overbrace{C_{20}H_{13},NO_4}$		Cyminylia. $\overbrace{C_{20}H_{13},H_2N}$	

he hydrocarbons enumerated in the first column of the fore- table are supposed to be hydrides of particular radicles. supposed radicles, viz., *phenyl* ($C_{12}H_5$), *toluyl* ($C_{14}H_7$), *xylyl*), *cuminyl* ($C_{18}H_{11}$), and *cyminyl* ($C_{20}H_{13}$), have not hitherto isolated. Their oxides, which would correspond to the ry ethers, are also unknown; compounds, however, have ormed, which appear to contain oxide of phenyl in combina- ith acids; such, for example, as the following :—

oate of phenyl . .	$C_{12}H_5O,C_{14}H_5O_3$	Laurent and Gerhardt.
ate of phenyl . . .	$C_{12}H_5O,C_4H_3O_3$?	Williamson and Scrugham.
phate of phenyl . .	?	
nate of phenyl . .	$C_{12}H_5O,C_{20}H_{11}O_3$	

nzol is a compound of considerable interest and importance. ongs to a group known as the *phenic* series. We shall, re, describe its properties, and that of some of its deriva- including carbolic acid, and shall afterwards proceed to briefly some of the other hydrocarbons, among which is *the most remarkable.*

1. *Benzol.—Phenic Series.*

(1358) **Benzol**; *Benzine* or *Phene* ($C_{12}H_6$); *Sp. gr.*
0·85 *at* 60°; *of vapour* 2·77.—This is a very limpid, c
liquid, of a peculiar and rather agreeable odour. If exp
cold of 32°, it solidifies in transparent crystals, grouped
leaves, or in masses resembling camphor, which melt at
boils at 177°, and emits a highly inflammable vapour, whi
with a white smoky flame, depositing large quantities of
If its vapour be transmitted through red-hot tubes it is
posed, and a large quantity of carbon is deposited. I
soluble in water, but is freely soluble in alcohol, ether, o
pentine, wood spirit, and acetone. When hot it dissolves
phosphorus, and iodine, and deposits the greater portion o
It is also an excellent solvent for caoutchouc and gutt
and on evaporation it leaves them with their peculiar phy
racters unaltered. Benzol also dissolves wax, camphor,
bodies with facility. Its solvent power for fats and oils
to be used with advantage for removing grease stains from
of silk or woollen. Benzol does not dissolve copal or re
facility, but if these bodies be exposed to its vapour at a h
perature they are gradually dissolved by it.

Benzol was originally obtained by Faraday from th
produced by the compression of oil gas, and was named *b*
of hydrogen. Subsequently the liquid procured by Mit
from the distillation of benzoic acid with an excess of lim
termed *benzine*, was found to yield the same body; HO
$+ 2\,CaO = 2\,CaO,C_2O_4 + C_{12}H_6$: and recently, Mansfield
tained it in large quantity from the more volatile portion
naphtha.* It may also be obtained, mixed with other
by several other processes, such as the distillation of phth
with lime, and the dry distillation of quinic acid. Ben
easily be procured in small quantities by exposing a mi
one part of benzoic acid with three parts of quicklime, to
rate heat gradually applied; the distillate should be agita
a weak solution of potash, and the benzol which rises to th
be dried by digestion upon chloride of calcium; after whi
be obtained pure by redistillation. Benzoic acid yields
third of its weight of benzol.† When benzol is required

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* Church found in light coal naphtha a hydrocarbon isomeric w
which he terms *parabenzol*; it boils at 207°.

† If benzoate of lime be distilled with one-tenth of its weight of
it yields a red liquid which, when submitted to redistillation,

quantity, its cheapest source is coal naphtha, although ll scale its purification is tedious. Mansfield, after puriby repeated rectifications, takes advantage of its power of g at 32°, in order to free it from the hydrocarbons which ny it, and which remain liquid at that temperature. By g in this way upon two gallons of naphtha, a pint of pure as procured.

9) *Hydrocarbons homologous with Benzol.*—*Toluol*, or , is one of the products of the distillation of balsam of d it appears to be identical with the *retinaphtha* obtained etier and Walter, from the distillation of rosin (1291). as found by Cahours, mixed with toluol, cumol, and cymol, the oils which are separated from crude wood spirit by the of water. *Cumol* may also be obtained by the distillation inic acid with an excess of quicklime : it appears to be idenith the *retinyl* of Pelletier and Walter. *Cymol* is present nce of cumin, and it may also be obtained by distilling r with anhydrous phosphoric acid, or with chloride of zinc. hydrocarbons are not, however, of sufficient importance to any lengthened description in this work. In the following eir boiling points and densities are compared with those of :—

Hydrocarbon.	Formula.	Boiling point ° F.	Specific Gravity.	
			Liquid.	Vapour.
Benzol . .	$C_{12}H_6$	177°	0·85	2·77
Toluol . .	$C_{14}H_8$	230°	0·87	3·26
Xylol . .	$C_{16}H_{10}$	263°		
Cumol . .	$C_{18}H_{12}$	299°		3·96
Cymol . .	$C_{20}H_{14}$	341°	0·861	4·59

60) *Other Compounds of Benzol.*—Benzol yields direct nds with chlorine and bromine, $C_{12}H_6Cl_6$ and $C_{12}H_6Br_6$, posed to the sun's light in contact with these halogens. ubstances present a certain analogy with Dutch liquid, and

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nd when the temperature rises to 599° a compound termed *benzone* or *none* ($C_{12}H_5.C_{14}H_5O_2$) passes over; this substance on cooling solidimass of straw yellow crystals, which may be purified by recrysfrom ether. When pure it forms beautiful colourless crystals, to the oblique system. It melts at 115°, and boils at 599°; it has ble ethereal odour. Benzo-phenone may be regarded as a combibenzoyl with phenyl; or as benzol, in which the place of an equivadrogen has been supplied by that of an equivalent of benzoyl. When h a mixture of hydrate of potash and lime, it is decomposed into benzoate of potash :—

$$C_{12}H_5,C_{14}H_5O_2+KO,HO = C_{12}H_5,H+KO,C_{14}H\,O_3.$$

when decomposed by an alcoholic solution of potash, yield compounds which contain $C_{12}H_3Cl_3$ and $C_{12}H_3Br_3$.

Sulphuric acid forms a compound acid with benzol, termed *hyposulphobenzidic* or *sulphobenzolic acid* ($HO,C_{12}H_5,S_2O_5$): it furnishes readily crystallizable salts. If benzol be treated with sulphuric anhydride a viscid mass is produced, which may be dissolved in a small quantity of water, but on the addition of a considerable amount of water, sulphobenzolic acid remains in the liquid, and a sparingly soluble crystalline body is separated. This crystalline body is termed *sulphobenzide* ($C_{12}H_5SO_2$); it may be purified by crystallization from ether: it is fusible at 212°, and may be distilled unaltered at a much higher temperature. Hofmann and Buckton have lately obtained a sulpho-acid with a larger proportion of sulphuric acid, termed *disulphobenzolic acid* ($2HO,C_{12}H_4S_4O_{10}$; p. 310), by heating benzonitrile with fuming sulphuric acid.

(1361) *Nitrobenzol* or *nitrobenzide* ($C_{12}H_5NO_4$), *Sp. gr. of liquid* 1·209; *of vapour* 4·4; *Fusing pt.* 37°; *Boiling pt.* 415°.—Benzol is remarkable for the facility with which it yields substitution compounds with peroxide of nitrogen. If benzol be added, in small portions at a time, to warm fuming nitric acid, it is dissolved, and on cooling, or on being diluted, is separated in the form of a yellow oil, which may be purified by washing, first with water, and then with a weak solution of carbonate of soda.

Nitrobenzol is a yellowish oil, which may be distilled unaltered; it crystallizes in needles when exposed to a temperature of 37°. It has a very sweet taste, and an odour resembling that of bitter almonds, which has led to its use in perfumery under the name of *Essence of Mirbane*. Nitrobenzol is soluble in alcohol and in ether, in all proportions. If its alcoholic solution be saturated with ammonia, and then with sulphuretted hydrogen, sulphur is deposited, and aniline is formed; aniline is also obtained from it still more readily by adding nitrobenzol to a mixture of equal parts of alcohol and hydrochloric acid, and introducing fragments of zinc, or by the process of Béchamp, with protacetate of iron (p. 446). The successive formation of nitrobenzol and of aniline may be employed as a test for the presence of benzol in oils:—a few drops of the suspected liquid are to be heated gently with fuming nitric acid in a test tube, and largely diluted with water, when oily drops of nitrobenzol are separated; if the liquid be agitated with ether, the nitrobenzol is dissolved, and may be decanted into a fresh tube: to this a mixture of equal parts of alcohol and hydrochloric acid are added, and a few fragments of granulated zinc. The nitrobenzol will thus be reduced to aniline, which may be liberated by the addition of potash in excess: it must be again agitated with ether to dissolve the aniline, and if this ethereal solution be mixed with a solution of chloride of lime, the violet tint characteristic of aniline will be developed.

Dinitrobenzol [$C_{12}H_4(NO_4)_2$].—If benzol be boiled with fuming nitric acid, or if it be allowed to fall, drop by drop, into a mixture of oil of vitriol and nitric acid so long as the liquids mix, dinitrobenzol is formed; the liquid must be boiled for a few minutes, and, on cooling, the dinitrobenzol is deposited in the form of a crystalline magma. It must be washed with water, and recrystallized from alcohol: it melts at a temperature below 212°. Dinitrobenzol represents benzol in which two equivalents of peroxide of nitrogen have taken the place of two equivalents of hydrogen. If its alcoholic solution be treated with hydrosulphate of ammonia, *a* nitraniline (page 452) is produced.

When dinitrobenzol is dissolved in alcohol, and treated cautiously with hydrochloric acid, after introducing a plate of pure zinc, no gas is given off, but a crimson solution is formed. On supersaturating with an alkali, and treating with alcohol, a beautiful orange-red substance, termed *nitrosophenylin* ($C_{12}H_6N_2O_2$), is obtained. It is easily soluble in acids and in alcohol, but nearly insoluble in water and in benzol. Compounds homologous with dinitrobenzol yield by similar treatment bodies corresponding with nitrosophenylin.

(1362) *Derivatives of Nitrobenzol obtained by reduction.*—Nitrobenzol experiences a reduction of a different kind if it be treated with an alcoholic solution of potash; *azoxibenzide* ($C_{12}H_5NO$) is then formed, and may be obtained by distilling the liquid until it separates into two layers; the upper oily one, when washed with water, yields brown needles of azoxibenzide; they may be purified by dissolving them in alcohol, and transmitting a current of chlorine (to destroy the colouring matter), and recrystallizing. The crystals thus obtained are of a sulphur yellow colour, and often exceed an inch in length. It is fusible at 97°. When distilled it yields aniline, and a new body termed azobenzol.

Azobenzol, or *Azobenzide* [$(C_{12}H_5N)_2$, *Fusing pt.* 149°; *Boiling pt.* 380°] may also be procured by distilling nitrobenzol with an alcoholic solution of potash; towards the end of the distillation, it passes over in the form of a red oil, which solidifies in large crystals: it may be purified by re-crystallization from ether, and may be obtained in the form of orange-coloured plates, which are freely soluble in alcohol, but scarcely so in water. It is obtained been clearly made out. If azobenzol be treated it yields two substitution compounds $[C_{24}H$ $C_{24}H_8(NO_4)_2N_2]$—the latter, when reduced by ammonia, yields another base, termed *diphenine* yellow colour; it is soluble in ether:—

$$\overbrace{C_{24}H_8(NO_4)_2N_2}^{\text{Dinitro-azobenzol.}}+6\,H_2S_2=2\,\overbrace{C_{12}H_6N_2}^{\text{Diphenine.}}+4\,H_2O$$

(1363) Phenic, or *Carbolic Acid; Hydrate o* $(C_{12}H_6O_2=HO,C_{12}H_5O)$: *Sp. gr. of liquid* 1·065; 95°; *Boiling pt.* 369°.—This substance is the acid product of the distillation of pit-coal. It by the distillation of the salicylates of the alkalies (1267). It is likewise found amongst the produ lation of gum benzoin, and of the resin of tl *hastilis.* Stædeler has found phenic acid in the and of some other animals.

Laurent obtains phenic acid from the oil of lecting separately those portions which boil at be 400°, and mixing with this oil a hot saturated sol of potash, adding a quantity of the powdered hyc separation of a white crystalline substance imn The liquid portion must be decanted, and the cry dissolved in a small quantity of water. When separates into two layers, the denser of which

esence of a minute trace of moisture is sufficient to cause
uefaction of the crystals. Phenic acid is very sparingly
in water, but is dissolved by alcohol, ether, and concen-
acetic acid in all proportions. It has a burning taste, and an
of smoke, resembling that of kreasote. Its vapour strongly
s the skin of the lips, and of the gums. Phenic acid pos-
antiseptic properties similar to those of kreasote: indeed,
of the commercial kreasote consists solely of phenic acid.
lutions do not redden litmus paper: a drop of it let fall
paper produces a transient greasy stain. If a splinter of
be dipped into a solution of phenic acid, and then into nitric
rochloric acid, the wood as it dries becomes blue.

henic acid, when heated with ammonia in a sealed tube,
es partially converted into water and aniline. The acid
ines with potash, and forms with it a crystalline com-
d; though it may be distilled, unchanged, from hydrate of
, and from quicklime or caustic baryta in excess. Phenates
hese bases may be obtained, but they are easily decom-
d.

(1364) *Homologues of Phenic Acid.*—Phenic acid is accompa-
in coal tar by other homologous bodies which greatly re-
le it. By subjecting commercial coal tar kreasote to frac-
ted distillation, Williamson obtained a liquid which boils at
°, and which is nearly insoluble in solution of ammonia.
liamson terms it *hydrate of oxide of cresyl* ($HO,C_{14}H_7O$); or
ight be termed *kresylic acid.* It is soluble in oil of vitriol,
ucing a violet colour, and forming a compound acid. This
tance is metameric with anisol (1277) and with benzoic alcohol
), and would be the phenic acid of the toluic series. When
d with fuming nitric acid, it is oxidized with almost explo-
violence, and a *trinitrokresylic acid* ($HO,C_{14}H_4(NO_4)_3O$),
ologous with carbazotic acid, is produced.

t has been suggested that the kreasote of wood tar (1351)
third homologue ($HO,C_{16}H_9O$), in which case it would be
henic acid of the xylylic series; but the difficulty of purifying
ote renders its exact composition a matter of uncertainty.

365) *Ethers of Phenic Acid.*—Phenic acid may be caused
ter into combination with the oxides of the alcohol radicles
cess of double decomposition, which consists in distilling
homethylate, sulphethylate, or sulphamylate of potash
nate of potash. These ethers may likewise be procured
g phenate of potash with the iodides of methyl, of ethyl,
yl; they are also produced by the distillation of the

salicylic ethers with caustic baryta, the preparation of ani the latter process being represented by the equation:—

$$\overbrace{C_2H_3O,C_{14}H_5O_5}^{\text{Salicylate of methyl.}}+2\,BaO=2\,BaO,C_2O_4+\overbrace{C_2H_3O,C_{12}H_5O}^{\text{Phenate of methyl.}}$$

Anisic acid, which is metameric with salicylate of methy yields phenate of methyl, which is identical with anisol.

The ethers of phenic acid may thus be contrasted with th itself:—

	Formula.	Boiling point.
Phenic or carbolic acid . . .	$H\ O,C_{12}H_5O$	370°
Phenate of methyl, or anisol .	$C_2\,H_3\,O,C_{12}H_5O$	306°
Phenate of ethyl, or phenetol .	$C_4\,H_5\,O,C_{12}H_5O$	342°
Phenate of amyl, phenamylol .	$C_{10}H_{11}O,C_{12}H_5O$	437°

Each of these ethers, when treated with nitric acid, substitution compounds analogous to those furnished by (1277), and when submitted to the action of hydrosulph ammonia, bases are obtained analogous to anisidine, nitran and dinitranisidine.

(1366) *Products of the Decomposition of Phenic Acid.*— phenic acid is distilled with perchloride of phosphorus, it *chloride of phenyl* ($C_{12}H_5Cl$), which is a colourless mobile with a fragrant smell, resembling that of bitter almon boils at 277°. At the same time *phosphate of phenyl* is f it may be obtained at a low temperature in beautiful c When melted, it is slightly yellow, and has a fluoresce perty. If terchloride of phosphorus be substituted for th chloride, chloride of phenyl and phosphite of phenyl are pro and the latter, when distilled, yields benzol amongst other pr (Williamson). Benzol, it will be remarked, contains two lents of oxygen less than phenic acid; the phosphorous this case deoxidizes the phenic acid, and becomes converte phosphoric acid.

Phenic acid gives rise by substitution to an unusual n of acid compounds, formed upon the type of phenic acid such for example as the following:—

Phenic, or carbolic acid	$HO,C_{12}H_5O$
Dichlorophenic, or chlorophenesic do. . .	$HO,C_{12}H_3Cl_2O$
Trichlorophenic, or chlorophenisic do. . .	$HO,C_{12}H_2Cl_3O$
Pentachlorophenic, or chlorophenusic do.	$HO,C_{12}\quad Cl_5O$
Bromophenic, or bromophenasic do. . .	$HO,C_{12}H_4BrO$
Dibromophenic, or bromophenesic do. .	$HO,C_{12}H_3Br_2O$
Tribromophenic, or bromophenisic do. .	$HO,C_{12}H_2Br_3O$

henic, or nitrophenasic acid . . .	$HO,C_{12}H_4(NO_4),O$
ophenic, or nitrophenesic do.. . .	$HO,C_{12}H_3(NO_4)_2,O$
ophenic, or nitrophenisic do. . .	$HO,C_{12}H_2(NO_4)_3,O$
ronitrophenic do.	$HO,C_{12}H_2Cl_2(NO_4),O$
o-nitrophenic do.	$HO,C_{12}H_2I_2(NO_4),O$
-dinitrophenic do.	$HO,C_{12}H_2Br(NO_4)_2,O$.

hese acids are monobasic, and form definite salts, many
ystallize very beautifully.

ure of chlorate of potash and hydrochloric acid con-
ic acid into trichlorophenic acid ($HO,C_{12}H_2Cl_3O$), and
ng the action, chloranile ($C_{12}Cl_4O_4$) is produced.

itriol dissolves phenic acid, without change of colour,
s a compound monobasic acid, termed *sulphophenic* acid
O,S_2O_6); it forms with baryta a soluble salt, which
in tufts of needles.

ic acid be allowed to fall, drop by drop, into fuming
it is attacked with great violence; each drop produces
ike that which accompanies the quenching of a hot
upon boiling the mixture, carbazotic (*trinitrophenic*)
$(NO_4)_3O$] acid is obtained. If the acid be more
ophenic acid [$HO,C_{12}H_4(NO_4)O$] or *dinitrophenic* acid
$(NO_4)_2O$] is produced. Both of these acids may readily
in crystals: most of their salts crystallize with facility;
resemble the carbazotates.

CARBAZOTIC, *trinitrophenic*, *nitro-phenisic*, or *picric*
$C_{12}H_2(NO_4)_3O$).—This is a frequent product of the
nitric acid upon complex organic substances. Phenic
n, coumarin, phloridzin, silk, indigo, and a variety of
it when treated with fuming nitric acid. The oil of
distils over at a temperature between 300° and 400°, is
best raw materials from which this acid can be procured.
f the *Xanthorrhœa hastilis* is also a convenient source
ic acid. In the latter case the resin should be purified
g it in alcohol, and evaporating the solution to dryness,
get rid of a woody fibre. Even when this precaution is
ic acid is formed in considerable quantity (Hadow).
ation obtained by acting upon these bodies with nitric acid
canted from the undissolved portions, and the carbazotic
is deposited as the liquid cools, may be purified by
h cold water, and converting it into a salt of ammonia,
be readily obtained in crystals; the carbazotate of
hen dissolved in boiling water may then be decom-
lute nitric acid, and crystals of carbazotic acid will be
the liquid cools. If boiled with caustic potash in

excess, the acid is decomposed, ammonia is expelled, and a brown resin is obtained in solution.

Carbazotic acid crystallizes in long, pale yellow, brilliant, rectangular plates, which are readily soluble in alcohol and in ether. It requires between 80 and 90 parts of cold water for its solution, forming a liquid of a bright yellow colour; it stains the skin yellow; if heated with a quantity of water insufficient to dissolve it, the acid melts to a yellowish transparent oil, which solidifies on cooling. The tinctorial power of this substance is so great that the aqueous solution may be diluted with several hundred times its bulk of water without losing its yellow colour. This acid has an intensely bitter taste, which has induced some persons fraudulently to substitute it in beer for a portion of the hops. Carbazotic acid is also employed for dyeing silk, to which it imparts a beautiful yellow colour, after the silk has been mordanted with alum, or with cream of tartar. On the application of heat carbazotic acid fuses to a yellowish oil, and if the temperature be gradually raised, it may be partially sublimed, but if suddenly heated it is decomposed with explosion. Concentrated sulphuric and nitric acids dissolve it unaltered, and deposit it on dilution. The carbazotates generally crystallize with facility; they are bitter and of a yellow colour: when heated they are decomposed with explosion. Carbazotate of *potash* is anhydrous; it is freely soluble in boiling water, but requires 260 parts of cold water for solution. The salt of *ammonia* is also anhydrous, but it is more soluble in water, and is somewhat soluble in alcohol. The *soda* salt is readily soluble in cold water. The carbazotates of the alkaline earths, and of lead and silver, are freely soluble.

Chloropicrine [$C_2Cl_3(NO_4)$ *Sp. gr.* 1·665] is the name given to a colourless transparent oil, of high refracting power, of a very penetrating odour resembling that of oil of mustard; it boils at 248°: its vapour is not inflammable. This substance is produced by the action of chlorinating agents upon carbazotic acid. It is easily obtained by distilling the acid from chloride of lime, and rectifying the oil which comes over from caustic magnesia. Alcoholic solutions of the alkalies decompose it into a chloride and a nitrate.

When the nitrous derivatives of phenic acid are submitted to the reducing action of hydrosulphate of ammonia two red amidated acids are produced. The compound obtained from dinitrophenic acid is termed *nitro-phenamic* acid [$HO,C_{24}H_{11}(NO_4)_2N_2O_3 + 4\ Aq$]; that from carbazotic acid is named *picramic* acid [$HO,C_{12}H_4(NO_4)_2NO$].

(1368) *Oxyphenic Acid*, or *Pyrocatechin* ($C_{12}H_6O_4$) is a sub- nce which may be noticed in connexion with phenic acid. direct relation has been traced between these two acids, but formula of oxyphenic differs from that of phenic acid by two ivalents of oxygen. Oxyphenic acid is obtained most abun- ntly by the distillation of catechu (1158), of moritannic acid, of gum ammoniacum; the acid liquid which passes over during operation must be decanted from tarry matters which accompany and be left to spontaneous evaporation. The crystals which are dually deposited must be freed from the mother liquor by pres- e between folds of filtering paper, and purified by sublimation. Oxyphenic acid crystallizes in colourless rectangular prisms. very soluble in water and in alcohol, but is nearly insoluble ether. It has a bitter taste, but scarcely any acid reaction. crystals fuse between 230° and 240°, and the liquid enters into llition between 464° and 473°. Its solutions in the alkalies ome first green, then brown, and finally black, whilst oxygen bsorbed. Its most characteristic reaction is the dark green our which it produces on the addition of perchloride of iron; he addition of any alkaline solution this colour is changed to eep red. With acetate of lead it yields a white precipitate. ric acid decomposes oxyphenic acid, and oxalic acid is formed.

(1369) *Styphnic Acid* [$C_{12}H_3N_3O_{16}=2\ HO,C_{12}H(NO_4)_3O_2$].— composition of this acid is such that it has been supposed to the same relation to oxyphenic acid, that carbazotic acid does phenic acid. This view, however, is not very probable, since acid is dibasic, and it cannot be obtained from oxyphenic by the action of nitric acid upon it. It is the product of action of nitric acid (sp. gr. 1·20) upon certain gum resins, as ammoniacum, assafœtida, and sagapenum. The aqueous acts of Brazil-wood and of the *Morus tinctoria* also yield it treated with nitric acid. Many of these substances furnish henic acid by distillation; extract of Brazil-wood yields it dantly by this process. Styphnic acid is sparingly soluble in water, but readily so in alcohol and in ether. It crystallizes ong prisms, which have a yellow colour. Its solution stains skin permanently yellow. Styphnic acid reddens litmus, and mposes the alkaline carbonates with effervescence. It also metallic iron and zinc with facility. Its taste is some- tringent, but not acid. The styphnates, like the carbazo- e decomposed with explosion, when gently heated. This ms two classes of salts, a neutral and an acid one: its salts *crystallize readily*.

2. *Naphthalic Series.*

(1370) NAPHTHALIN ($C_{20}H_8$): *Sp. gr. of solid* 1·153; *of vapour* 4·528; *Fusing pt.* 174°; *Boiling pt.* 428°.—This substance derives its principal interest from the important researches to which it was submitted by Laurent, and upon which chiefly he founded his theory of substitutions. Naphthalin is a constituent of the principal varieties of tar, but it is most abundant in coal tar, particularly in that obtained from the London gas-works. It is also produced when olefiant gas, phenic acid, and some other constituents of coal tar, are transmitted slowly through red-hot tubes. Naphthalin is easily obtained from the last portions of the distillate from tar, which become semisolid on cooling. The liquid constituents of this mass must be separated from it by pressure, and after recrystallization from hot alcohol it may be obtained perfectly pure by sublimation.

Naphthalin forms flaky crystals, consisting of rhombic plates, which feel unctuous to the touch and have a pearly lustre: its odour is peculiar and its taste biting and somewhat aromatic. It gradually undergoes sublimation at ordinary temperatures, and is easily distilled over with the vapours of water. Naphthalin does not readily take fire, but when kindled it burns with a white smoky flame. It is insoluble in water, but is readily soluble in alcohol, ether, oil of turpentine, and the fixed oils. Potash is without action upon it.

(1371) *Action of Sulphuric Acid upon Naphthalin.*—Sulphuric acid when heated with naphthalin combines with it. If the naphthalin be in excess, the acid forms with it a neutral fusible compound, termed *sulphonaphthalin.* If the sulphuric acid be in excess, and the temperature do not exceed 200°, a semisolid acid compound is formed, the *sulphonaphthalic.* If a higher temperature be employed, especially if fuming sulphuric acid be used, *Disulphonaphthalic acid* is also formed; it is a brown deliquescent compound, with a sour and bitter taste.

In all these cases the combination of hydrated sulphuric acid with naphthalin is attended with the separation of water; thus:—

Sulpho-naphthalin	$C_{40}H_{14}S_2O_6 = 2\,C_{20}H_8 + 2\,HO,S_2O_6 - 2\,H_2O_2$.
Sulpho-naphthalic, termed also hyposulpho-naphthalic acid	$HO,C_{20}H_7S_2O_5 = C_{20}H_8 + 2\,HO,S_2O_6 - H_2O_2$.
Disulpho-naphthalic acid, (thio-naphtic, or hyposulpho-naphtinic acid)	$2\,HO,C_{20}H_6S_4O_{10} = C_{20}H_8 + 2(2HO,S_2O_6) - 2\,H_2O_2$.

Besides these two acids, a small quantity of a third acid is sometimes obtained, which is metameric with the sulpho-naphthalic; from latter, this new acid is distinguished by the difference in the t of heat upon its baryta salt, which when burned in open air ulders like tinder till the naphthalin is consumed, whilst the ho-naphthalate of baryta burns with a luminous flame. The ho-naphthalates are soluble in water, and many of them in ol also; they have a bitter, almost metallic, taste.

(1372) *Action of Nitric Acid upon Naphthalin.*—Nitric acid ks naphthalin slowly at ordinary temperatures, and con- it into a sulphur-yellow compound, termed *nitro-naphthalin* $H_7(NO_4)]$; at higher temperatures *dinitro-naphthalin* $[C_{20}H_6$ $)_2]$ and *trinitro-naphthalin* $[C_{20}H_5(NO_4)_3]$ are produced. e different varieties of nitro-naphthalin crystallize beautifully their alcoholic or their ethereal solutions. When solu- of these compounds are exposed to the reducing action of sulphate of ammonia, each compound yields an azotised ; *naphthalidine, naphthylia,* or *naphthylamine* $(C_{20}H_9N)$ being furnished from nitro-naphthalin, and *semi-naphthalidam* or *phthylia* $(C_{20}H_{10}N_2)$, from dinitro-naphthalin; a third base was ed by Laurent from trinitro-naphthalin.* By prolonged ng with nitric acid, naphthalin is converted into a mixture of c and phthalic acids:—

$$\overbrace{C_{20}H_8}^{\text{Naphthalin.}}+4\,O_4 = 2\,\overbrace{HO,C_{16}H_4O_6}^{\text{Phthalic acid.}}+2\,\overbrace{HO,C_4O_6}^{\text{Oxalic acid.}}.$$

Phthalic, or *Naphthalic Acid* $(2\,HO,C_{16}H_4O_6)$, is produced by long-continued action of nitric acid upon naphthalin, as well upon the bichloride of naphthalin, and upon alizarin. The r mode of its production is interesting, since it indicates a exion between naphthalin and the colouring matter of madder. vaporating the solution obtained by acting upon naphthalin boiling nitric acid, phthalic acid is deposited in groups of llar crystals. It is sparingly soluble in cold water, and very le in alcohol and in ether. When exposed to a high tempe- re, water is expelled, and phthalic anhydride is sublimed. ill further prolonging the action of nitric upon phthalic acid, a *phthalic* acid $[2\,HO,C_{16}H_3(NO_4)O_6]$ may be procured. If lic acid be distilled with lime, carbonate of lime and benzol he results:—

$$2\,\overbrace{HO,C_{16}H_4O_6}^{\text{Phthalic acid.}}+4\,CaO = 2\,(2\,CaO,C_2O_4)+\overbrace{C_{12}H_6}^{\text{Benzol.}}.$$

A beautiful blue colour, rivalling that from aniline, has lately been d by oxidation of one of these bases.

Phthalic acid is dibasic, and Hofmann has suggested that it may form one member of a series of acids which would bear the same relation to the monobasic aromatic acids as the dibasic acids of the oxalic series bear to the volatile fatty acids; and he has obtained from cuminic acid, by the oxidizing influence of nitric acid upon it, a compound which, from its sparing solubility, he has termed *insolinic acid*. This acid is also dibasic. The two classes of acids would be represented thus—insolinic acid having, as yet, no representative in the monobasic series:—

Aromatic monobasic acids. $HO,C_{2n}H_{2n-9}O_3$.		Corresponding dibasic acids. $2\,HO,C_{2n}H_{2n-12}O_6$.	
Benzoic	$HO,C_{14}H_5O_3$	. . . .	?
Toluic	$HO,C_{16}H_7O_3$	Phthalic . . .	$2\,HO,C_{16}H_4O_6$
. . . .	?	Insolinic . . .	$2\,HO,C_{18}H_6O_6$
Cuminic	$HO,C_{20}H_{11}O_3$	. . . .	?

(1373) *Action of Chlorine on Naphthalin.*—When chlorine is brought into contact with naphthalin, the two bodies enter into direct combination: the naphthalin fuses, and a mixture of two compounds, presenting considerable analogy to Dutch liquid, is formed. One of these compounds has been termed, somewhat inappropriately, *chloride of naphthalin* ($C_{20}H_8Cl_2=C_{20}H_7Cl,HCl$), and the other, *bichloride of naphthalin* ($C_{20}H_8Cl_4=C_{20}H_6Cl_2,2\,HCl$). The formation of small quantities of substitution derivatives of naphthalin also usually accompanies the production of these compounds. It would have been more correct to have termed the first, *hydrochlorate of chlonaphtase*, and the second, *bihydrochlorate of chlonaphtese.* To avoid confusion, we shall, however, retain the terms of chloride and bichloride of naphthalin.

Chloride of Naphthalin ($C_{20}H_8Cl_2$) is an oily body, which is soluble in ether in all proportions. This circumstance is taken advantage of in effecting its partial separation from the bichloride, which is solid; but it is difficult to free it completely from this latter substance. *Bichloride of naphthalin* ($C_{20}H_8Cl_4$) exists in two modifications, which have been distinguished by the letters α and β. These modifications are both formed simultaneously during the action of chlorine upon naphthalin. The *bichloride* α is sparingly soluble in boiling ether, from which, on cooling, it is deposited in crystals; or it may be purified still more advantageously by crystallization from boiling oil of petroleum. It is scarcely soluble in alcohol. The *bichloride* β is very soluble in alcohol, and still more so in ether. It is obtained by exposing the ethereal mother-liquor, from which the bichloride α has crystallized, to a low temfor a few hours, and recrystallizing the deposit (which f a mixture of the modifications of α and β) from ether: l retains the modification β, which must be recrystallized crystals obtained are rapidly dissolved by cold ether. ıding compounds with bromine may be obtained, and other s also may be formed, into the composition of which both ınd bromine enter. (See Table below.)

the liquid chloride and the two modifications of the bi- of naphthalin are decomposed by distillation. When ith an alcoholic solution of potash, they are decomposed, f potassium is formed, and chlorinated derivatives of naph- produced. In each atom of these new compounds the f atoms of chlorine and hydrogen together is always 3, which is the number of atoms of hydrogen in the com- ım of naphthalin.

esearches of Laurent have disclosed the existence of an ex- numerous series of substitution compounds, formed upon f naphthalin, into the composition of which chlorine enters. sponding compounds with bromine may also be formed, ıer series may be obtained, in which the substitution is artly by chlorine and partly by bromine. It would be nt with the plan of the present work to attempt to give iled account of these bodies. The table which follows ate the composition of the principal compounds of this These bodies are of little practical importance, but their ion led Laurent to theoretical deductions regarding the constitution of chemical compounds generally, which ted a remarkable influence upon the recent progress of hemistry.* Many of these bodies are isomorphous.

1. *Chlorides and Bromides of Naphthalin.*

	1.	2.
loride of naphthalin	$C_{20}H_8.Cl_2$	$C_{20}H_7Cl,HCl$
f bronaphtase . .	$C_{20}H_7Br,Cl_2$	$C_{20}H_6BrCl,HCl$
of naphthalin . .	$C_{20}H_8,Cl_4$	$C_{20}H_6Cl_2$, 2 HCl
of chlonaphtase .	$C_{20}H_7Cl,Cl_4$	$C_{20}H_5Cl_3$, 2 HCl
romide of naphthalin	$C_{20}H_8,Cl_3Br$	$C_{20}H_6Cl_2$, HCl, HBr
of chlonaphtese .	$C_{20}H_6Cl_2,Cl_4$	$C_{20}H_4Cl_4$, 2 HCl
of brónaphtese .	$C_{20}H_6Br_2,Cl_4$	$C_{20}H_4Cl_2Br_2$ 2 HCl
of chlonaphtese .	$C_{20}H_6Cl_2,Br_4$	$C_{20}H_4Cl_2Br_2$ 2 HBr
of chlorabronaphtese	$C_{20}H_6ClBr,Br_4$	$C_{20}H_4Cl\ Br_3$, 2 HBr
of bronaphtese .	$C_{20}H_6Br_2,Br_4$	$C_{20}H_4Br_4$, 2 HBr
of bromechlonaphtise	$C_{20}H_5Br_2Cl,Br_4$	$C_{20}H_3Br_4Cl$, 2 HBr
of bronaphtise .	$C_{20}H_5Br_3,Br_4$	$C_{20}H_3Br_5$, 2 HBr

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ames proposed by Laurent, extraordinary and uncouth as many of r, are yet well adapted to represent the numerous substitution to which they refer. In the case of naphthalin, the compounds in chlorine are indicated by the prefix *chlo*, and end with a syllable

The compounds enumerated in the foregoing table are susceptible of decomposition by means of an alcoholic solution of potash, which effects the removal of a certain portion of chlorine or of bromine, and the body which is left is one of those represented in the following table :—

2. *Compounds formed upon the type* ($C_{20}H_8$).

Chlonaphtase . .	$C_{20}H_7Cl$	Chlonaphtose . .	$C_{20}H_4Cl_4$
Bronaphtase . .	$C_{20}H_7Br$	Chlorebronaphtose	$C_{20}H_4Cl_2Br_2$
Chlonaphtese . .	$C_{20}H_6Cl_2$	Chloribronaphtose	$C_{20}H_4Cl_3Br$
Bronaphtese . .	$C_{20}H_6Br_2$	Bronaphtose . . .	$C_{20}H_4Br_4$
Chlonaphtise . .	$C_{20}H_5Cl_3$	Bromechlonaphtuse	$C_{20}H_3Br_2Cl_3$
Bronaphtise . . .	$C_{20}H_5Br_3$	Chlonaphthalase .	$C_{20}H_2Cl_6$
Chlorebronaphtise	$C_{20}H_5Cl_2Br$	Chlonaphthalise .	$C_{20}\ \ Cl_8$

From the results of this decomposition it appears probable that the formulæ given in the third column of the first table represent, more accurately than those of the second column, the true composition of the so-called chlorides and bromides of naphthalin, the names of which would require modification accordingly.

It must not, however, be supposed that the foregoing tables indicate all the combinations of chlorine with naphthalin which may be formed by substitution or otherwise. Many of these different compounds exist in several distinct modifications. There are, for example, no fewer than seven distinct forms of *chlonaphtese*, which Laurent has distinguished by the letters *a*, *c*, *ad*, *e*, *f*, *x*, and *y*; four of them, *a*, *c*, *f*, and *x*, are obtained by the distillation of the bichloride of naphthalin, and two of them, *ad*, and *e*, by treating the same compound with potash, and *y* is the result of the action of chlorine upon dinitronaphthalin.

a and *x* are liquid at ordinary temperatures, *c* crystallizes in needles, which fuse at 122°, *f* crystallizes in tables, fusible at 214°, *ad* crystallizes in needles, which fuse at about 85°, *e* fuses at 88°;

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in which the vowels *a*, *e*, *i*, *o*, and *u*, are intended respectively to indicate the displacement of 1, 2, 3, 4, or 5 atoms of hydrogen. In *chlo*naphta*se* 1 atom of hydrogen has been displaced by 1 equivalent of chlorine; in chlonaphtose, 4 atoms of hydrogen have been displaced by 4 of chlorine. If the number of atoms of hydrogen displaced exceed 5, a fresh syllable, such as *al*, is added to the word, and the vowels (beginning with *a*) are again employed as before. Thus to express the substitution of 6 atoms of hydrogen by 6 of chlorine, the term chlonaphth*alase* is adopted. If bromine be the displacing body, the prefix *bro* is employed, and if both chlorine and bromine be present, the name employed indicates by the vowel in the concluding syllable the total number of atoms of hydrogen displaced, whilst the number of one of the halogens is indicated by a vowel attached to the prefix of the particular halogen to be represented. Thus *chloribronaphtose* indicates ($C_{20}.H_4Cl_3Br$), or a compound in which 4 atoms of hydrogen have been displaced by 3 atoms of chlorine, and by 1 of bromine: the name *bromechlonaphtose* indicates that the 4 atoms of hydrogen displaced are represented by 2 equivalents of bromine, and by 2 of chlorine.

y fuses at 203°, and may be sublimed in plates. Many of these bodies are also distinguished by differences in the degree of their solubility in alcohol and in ether, and by the different way in which they are attacked by chlorine and by bromine.

The existence of these remarkable modifications of chlonaphtese was accounted for by Laurent, on the supposition that in the compound ($C_{20}H_8$), or naphthalin, each of the 8 atoms of hydrogen has its distinct or allotted position in the compound molecule. In chlonaphtese 2 of these atoms of hydrogen are displaced by 2 equivalents of chlorine, but it is not a matter of indifference which of the atoms are thus displaced. Thus, if $\left\{C_{20}\begin{matrix}1. & 2. & 3. & 4.\\ 5. & 6. & 7. & 8.\end{matrix}\right\}$ represent the compound molecule of naphthalin, each numeral indicating a distinct atom of hydrogen, it is not a matter of indifference whether the displacement shall take place thus,

$$\left\{C_{20}\begin{matrix}1, & 2, & 3, & 4\\ 5, & 6, & Cl, & Cl\end{matrix}\right\} \text{ or thus } \left\{C_{20}\begin{matrix}1, & 2, & Cl, & Cl\\ 5, & 6, & 7, & 8\end{matrix}\right\} \text{ or thus } \left\{C_{20}\begin{matrix}1, & 2, & 3, & Cl\\ 5, & 6, & 7, & Cl\end{matrix}\right\}.$$

In all these cases we should still have compounds which on analysis would exhibit a perfectly similar composition; and yet, from the different relative position of the atoms of chlorine in the compound, the properties of each might be different. It may be shown by calculation, upon the principle of permutation, that twenty-eight such varieties of chlonaphtese are possible; of these seven have been discovered. This subject is placed in a very clear light by Gregory; (see also pp. 461, 462).

Chlonaphtise may also be obtained in seven different forms, all of which are crystallizable solids. *Chlonaphtose* is known under four different modifications. The compounds which contain both chlorine and bromine of the type *naphtose,* in which 4 equivalents of hydrogen have been displaced, may be formed in three different ways, and yield three metameric modifications, viz.:—1. *Chloribronaphtose,* which is obtained by exposing a mixture of bromine and chlonaphtise to the sun's rays; it forms six-sided prisms, which are fusible, and solidify at a temperature of about 221°. 2. *Bromachlonaphtose a,* which is obtained by passing a current of chlorine over heated bronaphtese: it forms six-sided prisms of the consistence of wax, which after fusion solidify at 230°. 3. *Bromachlonaphtose* β, which is obtained by the distillation of bichloride of bronaphtese; it forms flattened oblique prisms. Several modifications of many of the other chlorides might be enumerated, but it is unnecessary to particularize further. This great variety of form admits of explanation upon the hypothesis already applied to account for the different forms of chlonaphtese. It is obvious that numerous as are the modifications of many of the forms of these derivatives of naphthalin, they constitute but a small number of the possible varieties which a permutation in the relative position of the elementary atoms of the compound would allow.

(1374) *Paranaphthalin,* or *Anthracene* ($C_{28}H_{10}$ Anderson): *Sp. gr. of vapour* 6·741.—This substance accompanies naphthalin in the last stages of the distillation of coal tar. It may be purified from naphthalin by means of alcohol, which dissolves the naphthalin, but leaves almost all the anthracene untouched. Anthracene was supposed to be polymeric with naphthalin, but Anderson has lately shown that it possesses the formula given above: it is a white solid, which fuses at 416°. It may be distilled without being decomposed, and it condenses in lamellar crystals. Its best solvent is oil of turpentine. Chlorine acts slowly upon anthracene, forming a substitution compound ($C_{28}H_9Cl$). Chlorine also combines directly with anthracene forming the compound $C_{28}H_{10}O_2$; with bromine its combination has the formula $C_{28}H_{10}Br_6$. Treated with nitric acid it yields *oxanthracene* $C_{28}H_8O_4$ which crystallizes in long needles.

(1375) *Metanaphthalin* (the *retisterene* of Dumas) is compound polymeric with naphthalin: it was obtained by Pelletier and Walter during the distillation of resin. This body is sparingly soluble in cold alcohol, but is readily dissolved by boiling alcohol, as well as by ether, naphtha, and oil of turpentine. It fuses at 153°, and boils at 617°. It does not appear to form any coupled acid when treated with oil of vitriol.

(1376) During the distillation of the bituminous shale of Dorsetshire various products are obtained, which greatly resemble those contained in coal tar. The hydrocarbons approach in composition to $(C_2H)_{2n}$. A portion of the oil, which boils between 390° and 480°, furnishes a substance resembling kreasote, which Laurent termed *ampelin:* it is soluble to a considerable extent in water, but the addition of a few drops of an acid or of the solution of certain salts causes the separation of the ampelin. Ampelin is decomposed when the attempt to redistil it is made. By treating the oils of schist with nitric acid, Laurent obtained an acid metameric with the salicylic, and which he termed *ampelic acid.*

Shale tar is particularly rich in basic substances. G. Williams has detected in it, in addition to pyrrol, ammonia, pyridine, picoline, lutidine, collidine, and parvoline; besides two other bases as yet but imperfectly examined, which have been termed *carmidine* and *vertidine.* It is remarkable that aniline is not present amongst these bases. (Q. J. Chem. Soc., vii. 97.)

The destructive distillation of bones, and of azotised animal ers generally, yields a substance commonly known as *Dippel's al oil.* This oil comes over accompanied by an aqueous d, charged with carbonate, hydrosulphate, and hydrocyanate mmonia. The oil itself is a complex mixture, consisting of a which is soluble in acids, and of an insoluble portion; the r constituting the larger part of the oil. In the portion le in acids various volatile bases are present, including ylia, ethylia, tritylia, tetrylia, and amylia,—aniline, pyridine, ine, lutidine,—and the substance termed *Pyrrol* by Runge. portion insoluble in acids contains benzol, and a mixture of al nitriles.

1377) *Pyrrol* (C_8H_5N): *Sp. gr. of liquid* 1·077; *of vapour* : *Boiling pt.* 271°.—This body has been carefully examined nderson (*Edin. Phil. Trans.*, xxi. 586). Its purification is ded with considerable difficulties. During the distillation of cid solution of the crude pyridine bases (1187), from Dippel's peculiarly fœtid oil is obtained, which is colourless at first, t becomes in a few days of a reddish colour, and ultimately y black. On subjecting this oil to fractionated distillation, siderable portion is obtained between 270° and 290°. If ted with dilute sulphuric acid and dried over sticks of potash, ay be obtained nearly pure by repeated rectification. In r to purify it perfectly, it should be digested in a copper flask 5 or 6 times its weight of caustic potash, allowing the liquid t distils to fall back into the flask. Gradually the pyrrol rs into combination with the potash, and the heat may be d nearly to redness without expelling any portion of the ol. The residue thus obtained in the retort, after any traces coline have been expelled by heat, when thrown into water is mposed, and pure colourless pyrrol rises to the surface.* This id has an odour faintly resembling that of chloroform, and a pungent taste. It becomes brown when exposed to the air. s insoluble in alkaline solutions, but is slowly dissolved by s. Its most remarkable reaction is the production of a pale colour, which gradually deepens to an intense carmine when linter of fir-wood moistened with hydrochloric acid is exposed he vapour of pyrrol. When a solution of pyrrol in a dilute

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* Schwanert finds pyrrol among the products of the dry distillation of ucate of ammonia ($H_4NO,C_{10}H_3O_5$), accompanied by a substance which rms carbo-pyrrolamide $C_{10}H_6N_2O_2$, the amidated compound of an unstable the carbo-pyrrolic, which readily breaks up into pyrrol and carbonic acid.

$$\overbrace{HO,C_{10}H_4NO_3}^{\textit{Carbo-pyrrolic acid.}} = \overbrace{C_8H_5N}^{\textit{Pyrrol.}} + C_2O_4.$$

acid is heated, a red flocculent substance is deposited, and the liquid, if not extremely dilute, becomes of a gelatinous consistence; a similar change occurs in the acid solutions at ordinary temperatures if left for a few days. Alcoholic solutions of pyrrol precipitate solutions of corrosive sublimate, and of chloride of cadmium, but not those of the metals in general.

The red substance obtained by the action of acids, is supposed by Anderson to have the composition of $C_{24}H_{14}N_2O_2$, being formed from pyrrol by the elimination of the elements of ammonia and the assimilation of water, thus: $3C_8H_5N + H_2O_2 = H_3N + C_{24}H_{14}N_2O_2$.

(1378) *Bitumen, Asphalt, and Petroleum.*—Closely connected with the products of destructive distillation are the different forms of bitumen, asphalt, and petroleum. Deposits of these substances are found in various localities, as, for example, at Trinidad, at Amiano and in some other parts of the north of Italy, and also on the borders of the Caspian Sea, where it occurs in beds of marl above coal measures.* It is likewise abundant at Rangoon, and in several other localities of the kingdom of Burmah, where the naphtha is obtained from a pale blue clay, soaked with oil, which rests upon roofing slate, beneath which is coal containing much pyrites. The *petroleum* from the last-named locality has been made the subject of examination by De La Rue and H. Müller. (*Proceed. Roy. Soc.*, viii. 221.) It is obtained by sinking wells about sixty feet deep, in which the liquid is collected as it oozes from the soil. At common temperatures it has the consistence of goose fat; it is lighter than water, and has usually a greenish-brown colour; it has also a slight, peculiar, but not unpleasant odour. It is composed almost entirely of volatile constituents, about 11 per cent. of which come off below 212°. The fixed residue does not amount to more than 4 per cent. if it be distilled in a current of superheated steam. About 10 or 11 per cent. of the volatile matters consist of a body fusible at 149° but which is solid at ordinary temperatures (paraffin). When the liquid portion is agitated with oil of vitriol, some of its constituents enter into combination with the acid, but the greater part remains unaltered by this agent. In the portion which combines with the acid, benzol, toluol, xylol, and cumol have been identified, and there are several basic substances which have not as yet been completely examined. The liquid from which the hydrocarbons of the benzol series have been removed by the action of oil of vitriol, after being rectified, constitutes *rock oil* or *naphtha*; it is a mixture of several hydrocarbons, and is the liquid in which potassium and sodium are preserved. In order to purify it for this purpose, the crude distillate must be agitated several times with a fifth of its bulk of oil of vitriol; after which the undecomposed hydrocarbon is to be well washed with water, and rectified from quicklime. This liquid requires about eight times its bulk of alcohol for solution, but it is soluble in all proportions in ether and in the volatile oils. Hot naphtha dissolves phosphorus and sulphur, but deposits the greater portion of these bodies on cooling. It also dissolves caoutchouc, camphor, and fatty and resinous bodies generally. Pelletier and Walter describe three components of naphtha; one, which is termed *naphtha*, boils at about 190°; and the second, termed *naphthene* ($C_{16}H_{16}$), boils at 239°; and the third, *naphthol*, at 374°. It is not improbable that all these bodies are polymeric multiples of the hydrocarbon CH.

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* Quite recently extremely copious springs and wells of mineral oil have been discovered in Pennsylvania, and in Canada in the vicinity of Toronto.

Asphalt is the term given to solid bitumen (961). The bitumens differ in the facility with which they are attacked by solvents. Generally they contain but little of any matter soluble in alcohol, but most of them are dissolved in great part by ether, and by oil of turpentine. When distilled they yield substances which resemble the paraffin oils in properties and consistence (1347).

CHAPTER X.

DERIVATIVES OF CYANOGEN—UREA—ORGANIC BASES OF ANIMAL ORIGIN—URIC ACID, PRODUCTS OF ITS DECOMPOSITION.

§ I. DERIVATIVES OF CYANOGEN.

(1379) In describing some of the compounds of cyanogen (416), allusion was made to some important derivatives of this body (containing iron, cobalt, platinum, sulphur, and some other elements), which perform the functions of salt-radicles, or bodies which in their mode of combination present a certain analogy with the halogens. In the present chapter some of these compounds will be described; urea and some organic bases of animal origin will next be examined, after which uric acid and its more important derivatives will be considered.

(1380) Hydrocyanic acid in its anhydrous form combines with several of the anhydrous electro-negative chlorides, such as perchloride of iron, bichloride of tin, bichloride of titanium, and perchloride of antimony, and forms compounds, the composition of which is represented by the formulæ $(2HCy,Fe_2Cl_3)$; $(HCy,SnCl_2)$; $(HCy,TiCl_2)$; and $(3\ HCy,SbCl_5)$; but these compounds are all decomposed by water, and have no practical applications.

The general properties of the cyanides have been already discussed; some of these salts are of considerable practical importance, and may be now briefly described.

(1381) *Cyanide of Potassium* (KCy).—This salt is prepared in considerable quantities for the purpose of dissolving the salts of gold and silver in the processes of electrotyping; it is also employed in photography. It may be obtained by heating to dull redness, in a covered iron crucible, a mixture of 8 parts of anhydrous ferrocyanide of potassium, and 3 of dried carbonate of potash, until the fused mass has lost its yellow colour, and ceases to give off bubbles of gas. The iron is separated in the form of a metallic powder, and subsides to the bottom of the crucible; the fused cyanide can then be poured off, and solidifies on cooling to a milk-white mass. The cyanide thus obtained is, however, always mixed with a portion of cyanate, the reaction being such as is shown in the following equation :—

$$2\ (K_2,FeCy_3) + 2\ KO,C_2O_4 = 5\ KCy + KO,CyO + Fe_2 + C_2O_4.$$

If the presence of the cyanate of potash be injurious, it may be got rid of by adding to the mixture of the carbonate and ferrocyanide, before fusion, one-eighth of its weight of charcoal, which at a red heat reduces the cyanate of potash to the form of cyanide: the fused salt, when decanted from the iron, will then have a black colour, owing to the presence of particles of unconsumed charcoal. If it is to be used in solution immediately, it may be dissolved in water and filtered; but if required in the solid form it may be purified by treatment with boiling alcohol, from which, after filtration, it crystallizes on cooling. Cyanide of potassium forms colourless cubes; it is deliquescent, has an alkaline reaction, and when moist emits an odour of hydrocyanic acid. It is highly poisonous.

Cyanide of potassium is a powerful and valuable reducing agent. The oxides of a large number of metals, including those of lead, copper, and iron, when thrown into the melted salt are immediately reduced to the metallic state, whilst cyanate of potash is formed. It may also be used in the laboratory as a reducing agent instead of black flux, in testing for arsenic (708). Solutions of cyanide of potassium dissolve iron, zinc, nickel, and copper, with evolution of hydrogen, whilst potash is produced. Silver and gold are also dissolved by the solution of cyanide of potassium, if air be allowed free access, and double cyanides of potassium with those metals are formed.

(1382) *Double Cyanides.*—Cyanide of potassium, when mixed with metallic solutions, occasions a large number of precipitates, which in the majority of instances are soluble in an excess of the cyanide of potassium; they generally form with it crystallizable double salts. The cyanides of the metals of the other alkalies and of the alkaline earths may be substituted for cyanide of potassium, and produce similar double cyanides. The double cyanides which are formed in these cases are of two kinds or classes. The double salts of the first class are comparatively unstable, and are decomposed by the addition of a diluted free acid, such as the hydrochloric. In such cases the cyanide of potassium is decomposed, hydrocyanic acid is liberated, and the insoluble metallic cyanide is precipitated. The double salts which the cyanides of zinc, nickel, manganese, copper, and silver form with cyanide of potassium belong to this class. When, for example, the double cyanide of nickel and potassium is decomposed by hydrochloric acid, the following reaction occurs, and cyanide of nickel is precipitated, since it is insoluble either in hydrocyanic or in hydrochloric acid:—

$$\mathrm{NiCy,KCy + HCl = NiCy + KCl + HCy.}$$

The alkalies do not occasion precipitates in the solutions of the double cyanides. When mixed with a solution of a metallic salt which, like acetate of lead or sulphate of copper, is capable of furnishing an insoluble cyanide, a double insoluble cyanide is formed, for example:—

$$\mathrm{NiCy,KCy + PbO,C_4H_3O_3 = NiCy,PbCy + KO,C_4H_3O_3.}$$

The cyanides of this class are highly poisonous. Many of these double salts, when mixed with other metallic solutions, exchange their potassium for the metal of the salt which has been added, and thus form double cyanides, which are insoluble in water, but are readily decomposed by dilute acids. Thus a double cyanide of zinc and of barium may be obtained by mixing a solution of acetate of baryta with one of the double cyanide of zinc and potassium; $\mathrm{ZnCy,KCy + BaO,C_4H_3O_3 = ZnCy,BaCy + KO,C_4H_3O_3}$; and a double cyanide of nickel and copper may be obtained by mixing a solution of the cyanide of nickel and potassium with one of sulphate of copper.

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logous to chlorine and the halogens, in consequence of wh
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The double salts which the cyanides of cobalt, of ir
chromium, and of platinum, form with cyanide of pota
belong to this class, and they contain compounds to whic
terms cobalticyanogen, ferrocyanogen, ferricyanogen, ch
cyanogen, and platinocyanogen, have been applied: these ra
are distinguished by the property of yielding compounds
hydrogen which possess acid characters, and contain a c
number of equivalents of hydrogen in the place of the pota
of the double cyanide. For instance, the double cyan
potassium and iron, termed yellow ferrocyanide of potassium
be represented by the formula (K_2FeCy_3); it yields, when d
posed by hydrochloric acid, a compound termed hydro-ferro
acid ($H_2,FeCy_3$), which contains 2 atoms of hydrogen inst
the 2 of potassium in the yellow salt:—

$$K_2,FeCy_3 + 2\,HCl = \overbrace{H_2,FeCy_3}^{\text{Hydroferrocy. acid.}} + 2\,KCl.$$

The quantity of cyanogen in the simple cyanides may
termined by the following method proposed by Heisch
Chem. Soc., ii. 219). The substance for analysis is placed
small flask with some pieces of pure zinc in a little water; th
of the flask is fitted with a cork, through which are passed
funnel, and a second tube bent twice at right angles for ca
off the gas which is disengaged; sulphuric acid is poured in
funnel, and hydrogen is liberated; this gas at the moment
formation combines with the cyanogen, and carries it off
form of hydrocyanic acid, which is arrested by causing it t
through a solution of nitrate of silver. The cyanide of si
afterwards collected upon a filter and weighed, but it is bet
practised by Liebig, to conduct the vapours of hydrocyanic ac
a solution of potash, and afterwards to add to the alkaline
(410) a standard solution of nitrate of silver, or sulphate of

(a) *Cyanides which do not contain Electro-negative Metallic Cy*

(1383) The following are some of the principal in llic cyanides which yield double cyanides of the first class, double salts, which are decomposed, and yield a precipitate he addition of a dilute acid.

Cyanide of zinc is white, and insoluble in water; with cyanide otassium it forms a soluble salt (ZnCy,KCy), which may obtained in large, regular, anhydrous, colourless octohedra. *ide of zinc and sodium* (2 ZnCy,NaCy + 5 Aq) may be ob-
d in brilliant plates, if cyanide of sodium be substituted for ide of potassium. *Cyanide of nickel* (NiCy) forms an apple precipitate, which is very soluble in cyanide of potassium, ing a salt (NiCy,KCy + Aq) which crystallizes in oblique boidal prisms of a yellow colour. *Cyanide of manganese* as a bulky reddish-white precipitate, on mixing a solution of alt of manganese with one of cyanide of potassium; it rapidly mes brown by exposure to the air. This cyanide is soluble xcess of cyanide of potassium, but the solution absorbs en, and gradually deposits oxide of manganese. *Subcyanide pper*, Cu_2Cy, is a white powder obtained by treating an acid ion of subchloride of copper with cyanide of potassium; it is le in the dilute acids. Sulphate of copper yields with ide of potassium a brownish-yellow precipitate (CuCy), which begins to give off cyanogen, and becomes converted into a le cyanide (Cu_2Cy,CuCy + 5 Aq). The same salt may be ined in bright green crystals by adding hydrocyanic acid solution of sulphate of copper. Cyanide of copper (CuCy) luble in excess of cyanide of potassium, with an evolution of ogen, and formation of subcyanide; the subcyanide forms two allized double salts (Cu_2Cy,KCy), and (Cu_2Cy, 3 KCy). The r is the more soluble salt of the two.

1384) *Cyanide of Silver* (AgCy = 134) is precipitated in dense e flocculi when hydrocyanic acid or cyanide of potassium is d to a solution of nitrate of silver. It is nearly insoluble in e nitric acid even at a boiling temperature, but it is soluble mmonia, and is decomposed by hydrochloric acid. When d gently it melts, and at a high temperature gives off gen, leaving a residue of a grey colour, which retains a on of cyanogen. Cyanide of silver is freely soluble in ions of the cyanides of potassium, sodium, barium, calcium, ntium. These solutions give no precipitate with solutions etallic chlorides; indeed, cyanide of silver is dissolved by lutions of the chlorides of the metals of the alkalies, and ths. It is also soluble *in a solution* of nitrate of silver, in *solutions of the* ferrocyanide and ferricyanide of

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(1383) The following are some of the principal yanides which yield double cyanides of the first class, le salts, which are decomposed, and yield a precipitate lition of a dilute acid.

de of zinc is white, and insoluble in water; with cyanide um it forms a soluble salt (ZnCy,KCy), which may ed in large, regular, anhydrous, colourless octohedra. *f zinc and sodium* (2 ZnCy,NaCy + 5 Aq) may be ob- brilliant plates, if cyanide of sodium be substituted for f potassium. *Cyanide of nickel* (NiCy) forms an apple cipitate, which is very soluble in cyanide of potassium, salt (NiCy,KCy + Aq) which crystallizes in oblique l prisms of a yellow colour. *Cyanide of manganese* bulky reddish-white precipitate, on mixing a solution of f manganese with one of cyanide of potassium; it rapidly rown by exposure to the air. This cyanide is soluble of cyanide of potassium, but the solution absorbs d gradually deposits oxide of manganese. *Subcyanide* Cu_2Cy, is a white powder obtained by treating an acid f subchloride of copper with cyanide of potassium; it is the dilute acids. Sulphate of copper yields with f potassium a brownish-yellow precipitate (CuCy), which s to give off cyanogen, and becomes converted into a anide (Cu_2Cy,CuCy + 5 Aq). The same salt may be in bright green crystals by adding hydrocyanic acid ion of sulphate of copper. Cyanide of copper (CuCy) in excess of cyanide of potassium, with an evolution of and formation of subcyanide; the subcyanide forms two d double salts (Cu_2Cy,KCy), and (Cu_2Cy, 3 KCy). The he more soluble salt of the two.

) *Cyanide of Silver* (AgCy = 134) is precipitated in dense culi when hydrocyanic acid or cyanide of potassium is a solution of nitrate of silver. It is nearly insoluble in ric acid even at a boiling temperature, but it is soluble nia, and is decomposed by hydrochloric acid. When ntly it melts, and at a high temperature gives off leaving a residue of a grey colour, which retains a f cyanogen. Cyanide of silver is freely soluble in of the cyanides of potassium, sodium, barium, calcium, tium. These solutions give no precipitate with solutions tallic chlorides; indeed, cyanide of silver is dissolved by lutions of the chlorides of the metals of the alkalies, and ths. It is also soluble *in a solution* of nitrate of silver, in *solutions of the* ferrocyanide and ferricyanide of potassium. When ferrocyanide of potassium is used as vent, a dirty blue precipitate of cyanide of iron is formed, liquid becomes strongly alkaline; $K_2FeCy_3 + 2\,AgCy =$ $2\,(AgCy,KCy)$. The *cyanide of silver and potassiu* $KCy = 199$) is anhydrous, and may be obtained in octo in six-sided plates. Occasionally it forms rhomboidal pr 1 Aq. This salt is freely soluble in water and in boilin It is extensively employed for electro-silvering, since its if mixed with an excess of cyanide of potassium and mitted to electrolysis, deposits silver in compact cohere (877).

(1385) *Cyanide of Mercury* (formerly called *Bicy Mercury*) ($HgCy = 126$).—This salt may be prepared dissolving the red oxide of mercury in dilute hydrocyani which the oxide is soluble with great facility, or by mixture of 4 parts of finely-powdered Prussian blue and oxide of mercury, also finely levigated, with 40 parts until the undissolved portion has acquired a full brow the filtrate on evaporation yields the cyanide of mercury. also be procured by boiling 2 parts of sulphate of mercu part of ferrocyanide of potassium and 8 of water:—

$$2\,K_2FeCy_3 + 3\,(2\,HgO,S_2O_6) = 6\,HgCy + 2\,(2\,KO,S$$
$$+ 2\,FeO,S_2O_6.$$

Cyanide of mercury crystallizes in anhydrous rectangul which are colourless and transparent. It has a nauseou taste, and is very poisonous. It requires about 8 part water for solution; it is less soluble in ordinary al nearly insoluble in absolute alcohol. Cyanide of merc composed when heated; if perfectly dry it yields cyan metallic mercury, and a residue of paracyanogen. If n bonic acid, ammonia, and hydrocyanic acid are produced

Cyanide of mercury dissolves the red oxide of mercu and forms an *oxycyanide* ($HgO,HgCy$) which crystallizes i it is sparingly soluble in cold water, and the liquid has a reaction. Cyanide of mercury does not give any prec oxide of mercury on the addition of a free alkali. Wh with sulphuric or hydrochloric acid it is decomposed, and hydrocyanic acid. It is also decomposed by sulphuretted Cyanide of mercury enters into combination with a grea of chlorides, iodides, bromides, cyanides, nitrates, and other salts, forming with them crystallizable double does not occasion precipitates when mixed with the sol

zinc, cobalt, nickel, manganese, and other metals which
anides insoluble in water, with the exception of the salts of
m ; from which it would appear that mercury has a stronger
for cyanogen than any of the metals, excepting palladium.

86) *Cyanide of Gold.*—The *protocyanide* ($AuCy = 222{\cdot}6$) is
y cyanide of gold which is accurately known. It may be
l by several methods; the simplest consists in adding a
of cyanide of potassium to a dilute solution of terchloride
, so long as a precipitate is occasioned. It is a lemon-
powder, composed of microscopic hexagonal plates. It is
osed by heat into cyanogen and metallic gold: boiling
ulphuric, and hydrochloric acids do not decompose it, and
gia acts upon it very slowly. It is soluble in hyposulphite
and in hydrosulphate of ammonia; but its most important
is cyanide of potassium, with which it forms a double salt
$KCy = 287{\cdot}6$): this compound crystallizes in colourless
octohedra, or in pearly scales. It may be obtained by
g either the cyanide of gold or the oxide of gold (pre-
l from the terchloride by ammonia) in a solution of
of potassium. Cyanide of gold is also soluble in a
of the ferrocyanide of potassium. The double cyanide
ise formed by dissolving finely divided metallic gold in a
of cyanide of potassium with exposure to the air. The
cyanide of gold and potassium is largely used for gilding
ns of the galvanic battery (878).* Copper and silver
may also be gilt by it without the aid of the battery, by
mersion; portions of copper or of silver being dissolved
the operation.

87) *Cyanide of Palladium* ($PdCy = 79{\cdot}2$).—Palladium has
powerful affinity for cyanogen; when a solution of a salt of
m is mixed with one of cyanide of mercury, a yellowish-
recipitate of cyanide of palladium is formed; this precipitate
dissolved by means of cyanide of potassium, with which
a double salt, which crystallizes in rhomboidal prisms
$dCy + 3\ Aq$).

nide of lead ($PbCy$) is white; it is insoluble in water, and
t form a double cyanide with cyanide of potassium; it is
e in an excess of a solution of this salt.

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tger recovers the gold from the spent gilding solutions by evapo-
m to dryness, mixing the residue with its own weight of finely
l litharge, and fusing the mass; the lead and the gold are reduced,
a metallic button, *which, when treated* with nitric acid, leaves the
e *form of a fine powder.*

(*b*) *Electro-negative Metallic*

(1388) *Cyanides of Iron.*—Little is
simple cyanides of iron. When cyanide of
protosulphate of iron free from peroxide, a r
partially soluble in acids is formed, whic
the *protocyanide* of iron (FeCy). This
by an excess of cyanide of potassium,
into the yellow ferrocyanide of potassium.
obtained by decomposing Prussian blue b
sulphuretted hydrogen appears not to be
as was originally supposed by Robiquet.
not been procured in a separate form.
chloride of iron is mixed with one of cyan
cyanic acid is liberated, chloride of pot
precipitate of hydrated sesquioxide of iron i
Fe_7Cy_9+18 Aq (1392), *Turnbull's blue* Fe
Fe_3Cy_4+4 Aq, which Gmelin terms *Prussia*
pound cyanides of iron.

(1389) 1. FERROCYANIDES.—The cya
combination with other cyanides, give
classes of compounds, which are represente
of potash, or *ferrocyanide of potassium*
the red prussiate of potash, or *ferri*
(K_3,Fe_2Cy_6).

Ferrocyanogen (hypothetical).	FeC_6N_3.
Hydro-ferrocyanic acid . .	$H_2C_6N_3Fe$
Ferrocyanide of potassium .	$K_2C_6N_3Fe+3$ H
Ferrocyanide of sodium . .	$Na_2C_6N_3Fe+12$
Everitt's white salt, or ferrocyanide of potassium and iron	$K\,C_6\,N_3Fe_2$, or $K_2C_{12}N_6Fe_4$
Ordinary Prussian blue . .	$C_{18}N_9Fe_7+18$
Basic Prussian blue . . .	$C_{18}N_9Fe_9O_3+x$
Ferrocyanide of potassium and barium	$KBaC_6N_3Fe+3$
Ferrocyanide of copper . .	$Cu_2C_6N_3Fe+x$
Ferrocyanide of potassium and copper	$KCu\,C_6N_3Fe+2$
Ferrocyanide of lead . . .	$Pb_2C_6N_3Fe+3$

Liebig considers that these two class
separate radicles, *ferrocyanogen* $(FeCy_3=$
$(Fe_2Cy_6=$Fdcy). The first of these radicl

asic; but neither of these bodies has been obtained in a separate n. The hypothesis of their existence, however, affords a convenient de of representing the composition of the double cyanides into ch they are supposed to enter, and greatly facilitates the study these salts, which are numerous and important. The preceding e shows the composition of some of the compounds of the ocyanogen series.

(1390) *Hydroferrocyanic acid* (H_2FeCy_3).—This compound was inally obtained by Porrett, by the decomposition of ferrocyanide otassium, by means of tartaric acid. A better plan consists orming a concentrated aqueous solution of the ferrocyanide, ing it to expel the air, and then allowing it to cool in a vessel ided with a good cork to exclude air. Ether is then added, an excess of hydrochloric acid, which has also been deprived ir by boiling. On agitating the mixture, chloride of potassium rmed and remains in solution, and white scales of hydroferro- ic acid are deposited; $K_2FeCy_3 + 2\,HCl = H_2FeCy_3 + 2\,KCl$. se crystals must be washed with a mixture of alcohol and ether, dried *in vacuo* over sulphuric acid. Liebig adds by degrees cold saturated solution of ferrocyanide of potassium, an equal me of hydrochloric acid; the white precipitate of hydro-ferro- ic acid thus obtained must be washed with hydrochloric acid, d *in vacuo* upon a tile, and caused to crystallize from its solution lcohol by the addition of ether.

Hydroferrocyanic acid is dibasic. When exposed to the air, lsorbs oxygen and becomes blue: its solution, when boiled, lves hydrocyanic acid and deposits a white insoluble matter taining both iron and cyanogen. This body becomes blue in air. It is probably a protocyanide of iron, and by exposure ir it absorbs oxygen, becoming converted into basic Prussian , which is a compound of sesquioxide of iron and of true Prussian ; $9\,FeCy + 3\,O = (Fe_7Cy_9 + Fe_2O_3)$.

(1391) *Ferrocyanide of Potassium*, or *Prussiate of Potash* $FeCy_3 + 3\,Aq = 184 + 27$).—This important salt is met with in merce nearly in a state of purity. It is formed when azotised ters are heated to redness with carbonate of potash and iron. also formed when a protosalt of iron is mixed with a solution potash supersaturated with hydrocyanic acid. It is manu- ured on a large scale by heating dried blood, horns, parings of s, and other animal matters containing nitrogen, with an equal ht of carbonate of potash, and about one-third of their weight on filings, in a covered iron pot. Part of the carbon and gen *escape in combination with* oxygen and with hydrogen as carbonic acid and ammonia, while another portion enters into combination with the potassium, and this when treated with water attacks the iron, forming a salt which may be obtained from its solution, in large lemon-yellow tabular crystals, which contain 3 equivalents of water. The salt is tough, and splits into laminæ with facility.

The reactions by which the ferrocyanide is produced are complicated. When animal matter is heated with potash and iron, cyanogen is formed, which enters into combination with the potassium forming cyanide of potassium; but the temperature employed, is too high to allow of the formation of ferrocyanide. A variable quantity of the iron is at the same time converted into sulphide, owing to the action of the sulphide of potassium (produced by the reduction of the sulphate of potash in the pearlash) upon the metal. When the mass is lixiviated, the cyanide of potassium contained in the mixture attacks both the metallic iron and the sulphide of iron, becoming converted into ferrocyanide in the following manner:—a solution of cyanide of potassium dissolves metallic iron with evolution of hydrogen, hydrate of potash being set at liberty, whilst ferrocyanide of potassium is formed; $6\,KCy + Fe_2 + 2\,H_2O_2 = 2\,(K_2FeCy_3) + H_2 + 2\,(KO,HO)$: and the action of cyanide of potassium upon the protosulphide of iron may be thus represented; $3\,KCy + FeS = K_2FeCy_3 + KS$. Protoxide of iron is also readily dissolved by a solution of cyanide of potassium, whilst ferrocyanide of potassium is formed as in the previous cases; $3\,KCy + FeO + HO = K_2FeCy_3 + KO,HO$. A knowledge of these reactions explains the formation of the ferrocyanide during the lixiviation practised in the course of the manufacture.

The iron in the ferrocyanide does not perform the part of a base; for when a solution of this salt is submitted to electrolysis, the iron accompanies the cyanogen to the negative electrode. The iron cannot be thrown down from an aqueous solution of the salt by the addition of any alkaline solution; but if the alkaline liquid be boiled with oxide of mercury the iron is separated in the form of hydrated sesquioxide.

Ferrocyanide of potassium is soluble in about 4 parts of cold water, and in 2 parts of boiling water; but it is insoluble in alcohol; the addition of a solution of potash to its aqueous solution causes the separation of a portion of the salt in crystalline flakes. Ferrocyanide of potassium is not poisonous; it has a saline bitterish taste. When heated to 212° it loses the whole of its water of crystallization, and crumbles to a yellowish-white powder. When heated to redness in closed vessels it fuses, and at a full and prolonged red heat undergoes partial decomposition, nitrogen being evolved, whilst cyanide of potassium and carbide of iron are obtained. When dried and heated with peroxide of manganese, cyanate of potash is formed (411).

Ferrocyanide of potassium, when distilled with sulphuric acid, furnishes abundance of hydrocyanic acid; the decomposition which attends the reaction has been already explained (*note*, par. 408). When heated with concentrated oil of vitriol, the salt is decomposed into carbonic oxide, and a mixture of the sulphates of potash, of ammonia, and of protoxide of iron (303). When fused with dry carbonate of potash the ferrocyanide furnishes a convenient source of cyanide of potassium (1381). Ferrocyanide of potassium is manufactured in large quantities for use in dyeing and calico-printing; it produces a beautiful bright blue colour, which, however, will not bear washing with alkaline solutions, or with soap. It is used also in the preparation of Prussian blue, as well as in the processes of electro-plating and electro-gilding. It is the source from which the compounds of cyanogen are usually obtained. An aqueous solution of ferrocyanide of potassium produces characteristic precipitates with many of the metallic salts; it is, consequently, extensively employed as a qualitative test for indicating the presence of metallic bodies in solution. The precipitate generally consists of a ferrocyanide of the metal by which the precipitate is occasioned; usually the 2 atoms of potassium in the ferrocyanide are displaced by 2 equivalents of some other metal, such as cobalt, nickel, copper, or lead, yielding precipitates, Co_2FeCy_3; Ni_2FeCy_3; Cu_2FeCy_3; Pb_2FeCy_3. These precipitates are apt to retain portions of the ferrocyanide of potassium, from which it is difficult to free them even by long-continued washing. In a few cases 1 atom only of the potassium in ferrocyanide of potassium is displaced by an atom of some other metal, with which it forms an insoluble precipitate, as happens when a salt of baryta is precipitated; the yellowish-white precipitate consisting of $(KBa,FeCy_3 + 3\,Aq)$. The insoluble ferrocyanides cannot be precipitated in alkaline solutions; the liquid, in all cases, should be slightly but distinctly acid. Many of these precipitates are white, such as those of zinc, cadmium, nickel, manganese, tin, lead, bismuth, antimony, silver, and mercury; with the exception of those of cadmium and manganese, they are insoluble in dilute hydrochloric acid. The most characteristic precipitates occasioned by ferrocyanide of potassium are the following:—With the salts of cobalt it gives a yellowish-green; with protosalts of iron a white, becoming blue; with *persalts of iron* a deep blue; with salts of copper a reddish-brown; and with salts of uranium it also gives a brown precipitate.

(1392) The most important of these insoluble ferrocyanides is the compound largely employed as a pigment under the name of *Prussian blue* ($Fe_7Cy_9+18\,HO=Fe_4Fcy_3+18\,Aq$). Whenever ferrocyanide of potassium is mixed with a soluble persalt of iron, this beautiful blue precipitate is produced; 2 atoms of the persalt, persulphate of iron, for example, and 3 atoms of ferrocyanide of potassium undergo decomposition, so that the place of the 6 atoms of potassium is supplied by 4 atoms of iron; sulphate of potash remains in solution, whilst the Prussian blue is precipitated:—

$$2\,\overbrace{Fe_2O_3,3\,S_2O_6}^{\text{Persulphate of iron.}}+3\,\overbrace{(K_2,Fcy)}^{\text{Ferrocy. potass.}}=3\,\overbrace{(2\,KO,S_2O_6)}^{\text{Sulph. potash.}}+\overbrace{Fe_4,Fcy_3}^{\text{Prussian blue.}}.$$

The composition of Prussian blue seems to be rather anomalous, but if taken as Fe_4Fcy_3, it corresponds to the sesquichloride ($Fe_4Cl_6=2\,Fe_2Cl_3$), since ferrocyanogen being a dibasic radicle, it requires 4 Fe instead of 2 Fe for its saturation.*

When large quantities of Prussian blue are required, Liebig recommends that 11 parts of crystallized protosulphate of iron be dissolved in water, and divided into two equal portions; one part is then to be mixed with 2 parts of hydrochloric acid, and chloride of lime is gradually to be added until the whole of the protoxide is converted into peroxide; it is then to be mixed with the other portion of the solution, and a solution of 10 parts of ferrocyanide of potassium is to be added. The compound thus obtained is not a pure substance. It may, however, be prepared in a state of perfect purity by mixing a solution of sesquichloride of iron with one of hydroferrocyanic acid (Williamson). Commercial Prussian blue is generally contaminated with alumina, and sometimes with chalk, plaster of Paris, and starch. It always retains a portion of ferrocyanide of potassium.

Prussian blue, as met with in commerce, occurs in cubical or irregular masses of a dark blue colour, which when pressed with a hard body acquire a coppery lustre resembling that of indigo. It is insoluble in water and in weak acids, and has neither taste nor smell. After it has been washed with dilute hydrochloric acid,

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* Gerhardt and Laurent, starting from the fact that iron is capable of entering into combination in two proportions, assume that it possesses two different equivalent numbers: $Fe=28$, and $fe=\frac{2}{3}\,Fe$ or 18·6; and supposing that the portion of the iron in Prussian blue which has displaced the potassium is in the form of fe, Prussian blue becomes a compound of the same order as ferrocyanide of potassium, and may be represented by the formula, fe_2, Fcy.

may, however, be rendered soluble by triturating it with one
th of its weight of crystallized oxalic acid. When this is
uted with forty or fifty parts of water, it forms a blue solution,
ich is used as a writing ink. Prussian blue is also soluble in
old solution of tartrate of ammonia, forming a violet-coloured
uid. It is decomposed when treated with alkalies or alkaline
bonates, oxide of iron being liberated, and ferrocyanide of the
aline metal remaining in solution. Oil of vitriol produces a
ite pasty mass when triturated with Prussian blue, but on the
ition of water sulphuric acid is separated, and the blue pigment
reproduced. Prussian blue is decomposed when heated with
centrated sulphuric, nitric, or hydrochloric acid: it is also de-
posed by the action of chlorine. When boiled with red oxide
mercury, cyanide of mercury is produced and sesquioxide of iron
eparated.

Prussian blue contains water, which cannot be expelled by
without decomposing the compound. If heated in the open
it becomes kindled on the approach of an ignited body, and
ns like tinder, leaving a residue of peroxide of iron.

Soluble Prussian blue may be obtained by pouring perchloride
iron into an excess of ferrocyanide of potassium; the precipi-
te is insoluble in the saline liquid, and in solutions of salts gene-
lly, but it is freely soluble in pure water.

(1393) When protosalts of iron are mixed with a solution of
cyanide of potassium, a greenish-white precipitate is formed,
h appears to be the same as Everitt's white salt (408), and
y be regarded as a compound of cyanide of iron and ferrocyanide
potassium; $2\,K_2FeCy_3 + 2\,FeCl = (K_2FeCy_3 + Fe_2FeCy_3) +$
KCl. When this white substance is exposed to the air, the cyanide
iron becomes oxidized and turns blue, and a compound is formed
ed *basic Prussian blue*; it consists of one atom of sesquioxide
iron combined with one of Prussian blue: the ferrocyanide of
ssium originally present in the white compound may then be
hed away. The change which occurs is probably the following,
lecting the ferrocyanide of potassium of the precipitate, as it
not affected; $3\,Fe_2FeCy_3 + 3\,O = (Fe_7Cy_9 + Fe_2O_3)$. A strong
d removes the sesquioxide of iron from basic Prussian blue, and
verts it into ordinary Prussian blue.

94) 2. FERRIDCYANIDES, or *ferricyanides.—Ferricyanide of*
um, or *Red Prussiate of Potash* ($K_3,Fe_2Cy_6=329$).—When
of chlorine gas is passed through a dilute solution of
e of potassium, the liquid quickly changes colour
s *of a deep red*. *If* the current of the gas be

arrested so soon as the liquid ceases togive a blue precipitate with the persalts of iron, the solution on evaporation yields magnificent ruby-red crystals of ferricyanide of potassium. In this process the reaction which occurs is the following: $4(K_2FeCy_3)+Cl_2=2(K_3 Fe_2Cy_6)+2 KCl$. The chlorine acts by withdawing one-fourth of the potassium contained in the yellow salt; cloride and ferricyanide of potassium being the result. The erricyanide may be obtained by a second crystallization in transparent anhydrous right rhombic prisms of a beautiful red colour; and if the operation be performed on a large scale these crystals often attain a large size: they are soluble in about 2½ parts of cold water and in 1½ part of boiling water, but are insoluble in alcohol. If the action of the chlorine upon the ferrocyanide of potassium be too long continued, the red salt is in its turn partially decomposed, and a green compound is formed which interferes with the crystallization of the red salt. This green compound, according to the analysis of Pelouze, may be represented by the formula $(FeCy,Fe_2Cy_3+4 Aq)$, or it is the *magnetic cyanide,* corresponding to the magnetic oxide of iron. Ferricyanide of potassium is prepared on the large scale for the use of the calico-printer; but it is then generally obtained by decomposing the solid yellow salt by exposing it in powder to the action of a current of chlorine gas. Ferricyanide of potassium may also be obtained in small quantities by decomposing a solution of the yellow ferrocyanide by means of the voltaic battery in a diaphragm cell (867); it is formed in the solution at the positive electrode. It may also be obtained by acting upon the yellow prussiate by various oxidizing agents.

A solution of ferricyanide of potassium when mixed with an excess of potash furnishes a liquid possessed of considerable oxidizing power; it converts the hydrated protoxides of manganese, lead, and tin into peroxides of these metals, whilst the ferricyanide passes into the condition of ferrocyanide of potassium; $2(K_3,Fe_2Cy_6)+4(KO,HO)+2 MnO,S_2O_6=4 (K_2,FeCy_3)+2 KO,S_2O_6+2 MnO_2+2 H_2O_2$. The same solution is employed by the calico-printer for the purpose of discharging the blue colour of indigo from calico (Mercer). The red prussiate burns with scintillation when introduced into the flame of a candle. Ferricyanide of potassium produces a large number of insoluble compounds when mixed with the salts of many of the metals; and as the colours of these precipitates are often characteristic, this salt is frequently employed in the laboratory as a qualitative test for the metals in neutral or feebly acid solutions. With salts of zinc it gives an orange precipitate, with those of cadmium a yellow, with nickel a

-green, with cobalt a dark reddish-brown, with copper a green, with protosalts of iron a brilliant blue, with man- brown, with protosalts of tin a white, with silver an nd with subsalts of mercury a brownish red. These pre- with the exception of those with zinc and tin, are inso- dilute hydrochloric acid. The following table exhibits osition of some of the ferricyanides :—

ogen (hypothe-	$C_{12}N_6Fe_2$	Fdcy
ricyanic acid .	$H_3C_{12}N_6Fe_2$	H_3,Fdcy
ide of potassium	$K_3C_{12}N_6Fe_2$	K_3.Fdcy
ide of sodium .	$Na_3C_{12}N_6Fe_2+2\ HO$	Na_3.Fdcy + 2 Aq
ide of sodium tassium . .	$K_3Na_3C_{24}N_{12}Fe_4+12\ HO$	K_3Fdcy,Na_3Fdcy + 12 Aq
ide of potas- d barium .	$KBa_2C_{12}N_6Fe_2+6\ HO$	KBa_2,Fdcy + 6 Aq
ide of iron ull's blue) .	$C_{12}N_6Fe_5+x$HO	Fe_3,Fdcy + xAq

cyanide of potassium gives no precipitate in the solutions rsalts of iron, but a splendid blue when mixed with those otosalts. It is a very delicate test for protoxide of iron olution. If protosulphate of iron be employed, the change curs is the following: $2\ (K_3,Fdcy) + 3(2FeO,S_2O_6) = 2\ (Fe_3,$ $3\ (2\ KO,S_2O_6)$. The precipitate which is thus formed con- a highly valued and brilliant variety of Prussian blue, ially known as *Turnbull's Blue*. Turnbull's blue may be shed from ordinary Prussian blue by the action of a solution upon it, which decomposes it into ferrocyanide of potassium *netic* oxide of iron, whilst the ordinary blue when similarly yields ferrocyanide of potassium and sesquioxide of iron. liamson finds that when Everitt's white salt ($KFe,FeCy_3$) d with chlorine or with nitric acid it is decomposed, and a is formed (KFe_2,Fe_2Cy_6) corresponding in composition to l's blue, but containing an atom of potassium in the one of the atoms of iron. The formation of this substance effected by boiling the white precipitate with nitric acid, with twenty parts of water; as the liquid approaches the point a copious evolution of binoxide of nitrogen occurs: ns of the white salt lose one atom of potassium, and the ide of potassium and iron is formed. Care is required to the action of the acid from proceeding too far, otherwise pound acquires a green colour, owing to the formation of magnetic cyanide of iron.

en this *blue compound is treated* with a solution of the ferro-

cyanide of potassium, it is reconverted into the original w
pound, and pure ferricyanide of potassium is obtaine
liquid, two atoms of the yellow salt losing an atom
sium, which is transferred to the blue compound; KFe_2,F
$(K_2,FeCy_3) = 2\,(KFe,FeCy_3) + K_3,Fe_2Cy_6$.

From the foregoing statements it will be seen tha
different blue compounds containing iron and cyanogen ma
cured. The composition of these bodies may be thus repres

Ordinary Prussian blue . .	$Fe_7Cy_9 + 18\,Aq$	$= Fe_4,Fcy_3 +$
Basic or soluble ditto . . .	$Fe_7Cy_9,Fe_2O_3 + x Aq$	$= Fe_4,Fcy_3,F$
Turnbull's blue, or ferricyanide of iron	$Fe_5Cy_6 + x Aq$	$= Fe_3,Fdcy +$
Williamson's blue, or ferricyanide of iron and potassium	$Fe_4KCy_6 + x Aq$	$= Fe_2K,Fdcy$

Hydroferricyanic Acid (H_3Fdcy).—This compound
obtained in reddish-brown deliquescent crystals, by evap
the liquid in which ferricyanide of lead has been decom
means of diluted sulphuric acid.

(1395) 3. NITRO-PRUSSIDES.—When the vapour, no
oxide of nitrogen, but of nitrous acid (NO_3) is transmitted
a solution of hydroferricyanic acid, it is absorbed, hydrocy
and a new acid, the *hydronitro-prussic* are formed :—

$$\underbrace{H_3,Fe_2Cy_6}_{\text{Hydroferricyanic acid.}} + NO_3 = \underbrace{H_2,Fe_2Cy_5NO_3}_{\text{Hydronitro-prussic acid.}} + HCy.$$

This acid may be obtained in crystals with 2 Aq. Ge
presents the compound as containing 1 atom of oxygen le
given in the foregoing formula. Their composition is still

The nitro-prussides were originally procured by the
process, recommended by Playfair, by whom these salts
covered (*Phil. Trans.*, 1849, p. 481) :—

Common nitric acid is to be diluted with an equal
water, and when cold, powdered ferrocyanide of potassiu
be added in the proportion of 270 parts of the anhydr
(5 atoms) to 422 parts (2 atoms) of the ferrocyanide. The
gradually assumes a brown colour, cyanogen and hydrocy
are liberated, whilst a brisk effervescence occurs, owing to th
of carbonic acid and nitrogen, and the salt is dissolved, fo
mixture of ferricyanide and nitro-prusside of potassiu
nitrate of potash; heat must be applied gradually to the
by means of a water-bath, until gas ceases to be evolved,
liquid, instead of giving a blue precipitate with a protosalt
produces a dark green or slate-coloured precipitate. It m
be allowed to cool, by which means a large quantity of ni

ash, mixed with a small proportion of oxamide will be sepa-
ed. The strongly-coloured mother liquor must next be neu-
lized with carbonate of potash or carbonate of soda, by which a
enish-brown precipitate is caused; and the liquid, after filtra-
, must be evaporated and allowed to crystallize. The soda
crystallizes more readily than the nitro-prusside of potassium,
ch is somewhat deliquescent, although an anhydrous salt.

Nitro-prusside of Sodium ($Na_2,Fe_2Cy_5NO_2+4\,Aq\,?=262+36$).
his salt crystallizes in fine prisms of a ruby-red colour, which
ire about 2½ parts of cold water for solution. Its solution is
mposed by exposure to the sun's rays, Prussian blue being
osited, whilst binoxide of nitrogen escapes. *Nitro-prusside of*
ium ($Ba_2,Fe_2,Cy_5NO_2+6\,Aq\,?$) crystallizes in fine octohedra of
ark red colour.

The nitro-prussides give a pale green precipitate with salts of
er, and a flesh-coloured precipitate with those of silver. With
of zinc a salmon-coloured precipitate is produced; with salts
ickel, a dirty white; with salts of cobalt, a flesh-coloured pre-
ate; and with protosalts of iron, a salmon-coloured precipi-
is formed. The persalts of iron, and the salts of lead, of
cury, and of tin, give no precipitates with the nitro-
ssides. Chlorine is without effect upon solutions of the nitro-
ssides; but they are decomposed when boiled with the alkalies,
of the iron being separated as a crystalline hydrated sesquioxide,
ht the solution becomes orange-coloured, owing to the formation
new compound containing both cyanogen and iron. They are
decomposed by boiling oil of vitriol. If their solutions be
led with oxide of mercury, binoxide of nitrogen is evolved and
ide of mercury is formed. Sulphuretted hydrogen also de-
poses them. The most delicate and characteristic test for the
o-prussides is the production of a magnificent purple colour
n mixed with solutions of the alkaline sulphides. This colora-
is extremely intense, and may be employed to indicate very
te traces either of a soluble sulphide or of a nitro-prusside.
colour, however, speedily disappears. It appears to be due to
formation of a double salt of the nitro-prusside with the sul-
of the alkaline metal. By boiling the liquid, nitrosulphide
on and of the alkaline metal is obtained.*

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sulphides of Iron.—A remarkable class of compounds may be
y the reaction of nitrite of potash and hydrosulphate of ammonia
lts of iron (Roussin, *Ann. de Chimie*, III. lii. 285). If to a mixture
of hydrosulphate of ammonia and nitrite of potash a solution of
te or of protochloride of iron be added drop by drop, keeping the
stantly agitated, it is found that on raising the liquid to the boil-

(1396) 4. **Cobalticyanides.**—When the cyanide of potassium is added to a salt of cobalt, it gives a reddish brown precipitate (CoCy), which is soluble in excess of cyanide of potassium. The double cyanide of cobalt and potassium (2 KCy,CoCy) thus obtained is decomposed on the addition of hydrochloric acid, and the cyanide of cobalt is precipitated; but if, previously to the addition of

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ing point, the blackish precipitate which is at first formed is almost entirely redissolved. If the solution be boiled for a few minutes and then filtered, an extremely dark liquid runs through; this, on cooling, deposits hard, sandy, or needle-shaped crystals; the supernatant liquid presents only a slightly yellow tint. If a salt of the sesquioxide of iron be substituted for one of the protoxide, a similar result is obtained, but a considerable quantity of sulphur is left upon the filter.

The crystals thus formed are well-defined oblique prisms with a rhombic base. They are black and opaque, very heavy, sparingly soluble in cold water, but soluble in twice their weight of boiling water. Alcohol, wood-spirit, fousel oil, and concentrated acetic acid also dissolve them freely, but they are absolutely insoluble either in chloroform or in bisulphide of carbon. The effect of ether upon them is remarkable; they instantly become liquid if exposed to the vapour of ether, and are soluble in ether in almost unlimited quantity. Traces of ether or of alcohol in chloroform can be detected with certainty by agitating the specimen under trial with a few of the crystals. If pure the liquid will remain absolutely colourless, but the presence of one part of alcohol or of ether in 1000 will yield a coloured solution. These crystals have a brilliant metallic lustre: their taste is at first inky, followed by a persistent bitterness. The new salt is permanent in air containing a trace of ammonia; but if the substance be in the least acid gradual decomposition ensues, and ruddy fumes are seen in the bottle. It is not decomposed by a temperature of 212°, but if the heat be gradually increased, it is resolved at a little below 280° into sulphur, sulphite of ammonia, nitric acid, and nitrate of ammonia, leaving a residue of sulphide of iron. When heated sharply it deflagrates, emitting white fumes, which have an odour like that of burning gunpowder. The concentrated mineral acids immediately decompose the nitrosulphide; but acetic, hydrochloric, and oxalic acids have no effect upon it.

Potash and ammonia when added to its aqueous solutions cause a deposition of the crystals, unaltered in composition, scarcely any of the compound being retained in the liquid. Chlorine and iodine decompose it, causing a separation of binoxide of nitrogen and of sulphur. It is also immediately decomposed by the red oxide of mercury with evolution of binoxide of nitrogen; with the peroxide of lead it yields nitrate of lead and sulphur; it is also decomposed by permanganate of potash; solutions of nitrate of silver, corrosive sublimate, sulphate of copper, and sesquichloride of iron decompose the solution of this compound with evolution of binoxide of nitrogen and precipitation of black sulphides. The protosulphate of iron is without effect upon it. With nitrate of lead it gradually deposits oblique rhomboidal prisms, which are sparingly soluble in water, soluble in ether, and deliquescent in its vapour. Roussin attributes to the black crystals the following formula, $Fe_3S_5H(NO_2)_2$:—

		By calculation.		By Expt.
Fe_3	=	84	or 37·33	37·36
S_5	=	80	35·55	35·54
$(NO_2)_2$	=	60	26·66	26·45
H	=	1	0·44	0·45
		225	100·00	99·80

The formula suggested for the compound by Roussin is ($Fe_2S_3NO_2$, $FeS,NO_2.HS$). The remarkable point in the composition of this substance, which has been called *binitrosulphide of iron*, is that the iron is not indicated by any of the usual tests of the metal, such as ammonia, ferrocyanide of potassium, or hydrosulphate of ammonia. If it be boiled with a concentrated solution of caustic soda, ammonia is disengaged in abundance, and crystallised hydrochloric acid, it be exposed to the air, it absorbs oxygen, potash is liberated, and cobalticyanide of potassium is produced :—

$$8(CoCy,2KCy)+2\ H_2O_2+O_4=4\ (K_3,Co_2Cy_6)+4(KO,HO).$$

After this change has occurred, the addition of hydrochloric acid causes no precipitate. The cobalticyanide of potassium corresponds in composition to the ferridcyanide of the same metal. A *hydrocobalticyanic* acid (H_3,Co_2Cy_6) may be obtained by decomposing cobalticyanide of copper with sulphuretted hydrogen.

Cobalticyanide of Potassium (K_3,Co_2Cy_6).—This salt was discovered by Gmelin. It crystallizes in yellowish flattened prisms, which are anhydrous, and isomorphous with those of ferridcyanide of potassium. It is sparingly soluble in water. This salt may be obtained either by dissolving cyanide of cobalt in an excess of cyanide

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sesquioxide of iron is deposited. The solution contains a new salt, which, on evaporation, is deposited in black, well-defined crystals, aggregated in inverted hollow square pyramids. This salt, *sulphuretted nitrosulphide of iron and sodium* ($3\ NaS.Fe_2S_3NO_2$) is soluble in a solution of soda, but insoluble in caustic potash or ammonia. It is decomposed by metallic solutions, and by iodine, with evolution of binoxide of nitrogen in a manner very similar to that in which the same compounds behave to the binitrosulphide of iron. Acids decompose the salt with facility at ordinary temperatures, and occasion the deposition of a red flocculent substance ($Fe_2S_3,NO_2,\ 4\ HS$?) which readily subsides, and should be washed with a weak solution of sulphuretted hydrogen. By prolonged washing it loses a portion of its sulphuretted hydrogen.

This substance is soluble in alcohol and in ether; when dry it becomes slowly decomposed, emitting fumes of binoxide of nitrogen and ammonia, and leaving a residue of sulphide of iron. It is soluble in solutions of the alkalies as well as in those of their carbonates and sulphides, producing salts analogous to the compound with sodium already described.

Nitrosulphide of iron ($Fe_2S_3NO_2$). This compound is obtained by decomposing the foregoing sodium compound ($3\ NaS,Fe_2S_3NO_2,$) by adding gradually dilute sulphuric acid to a boiling solution of the salt. Sulphuretted hydrogen is evolved in abundance, and the nitrosulphide of iron is precipitated in the form of a black heavy powder. It is insoluble in water, in alcohol, and in ether. It is permanent while moist, but if dried is gradually decomposed, with evolution of binoxide of nitrogen. When dry and freshly prepared it burns like tinder if touched with an ignited body. It is soluble in the alkalies, and in the sulphides of the alkaline metals forming a new class of salts. The sodium compound ($Fe_2S_3NO_2,NaS,HO$) is easily obtained as an intensely dark red crystalline substance of metallic lustre, by dissolving nitrosulphide of iron in sulphide of sodium, and allowing the solution to crystallize over sulphuric acid.

An interesting relation has been observed between the nitrosulphides and the nitroprussides. The crystals of both classes belong to the oblique prismatic system. If a solution of the nitrosulphide of iron and sodium be mixed with one of cyanide of mercury, sulphide of mercury is precipitated, and nitroprusside of sodium is obtained in solution. On the other hand, if nitroprusside of sodium in solution be mixed with an excess of an alkaline sulphide a magnificent purple colour is produced, which passes on boiling into a reddish green, and nitrosulphide of iron and sodium is formed, whilst sulphocyanide of the alkaline metal remains in solution.

The chief point of interest in these nitrosulphides of iron is the complete manner in which the presence of iron is masked, and rendered impossible of detection by the ordinary tests, the iron in these salts being apparently contained, as in the ferrocyanides, in the electro-negative portion of the compound.

of potassium, and exposing it to the air; or by dissolving hydrated oxide of cobalt by the aid of a gentle heat in a solution of potash, supersaturated with hydrocyanic acid; in both cases oxygen is absorbed:—

$$8(CoCy,KCy)+4\,KCy+4\,HCy+O_4=4(K_3,Co_2Cy_6)+2\,H_2O_2.$$

The corresponding salt of *sodium* ($Na_3,Co_2Cy_6+4\,Aq$) crystallizes in long, transparent, colourless needles; that of *baryta* in prisms with 6 Aq. Solutions of these cobalticyanides occasion precipitates in a large number of metallic salts. Cobalticyanide of zinc is white; that of nickel is gelatinous, and of a pale blue; that of cobalt is of a pale red; that of copper, of a pale blue; those of the protoxide of iron, manganese, and tin, and those of silver and of suboxide of mercury, are white: salts of lead give no precipitate with the soluble cobalticyanides.

(1397) 5. CHROMICYANIDES.—Salts of the green oxide of chromium yield with cyanide of potassium a pale bluish grey precipitate (Cr_2Cy_3), which is not soluble in excess of cyanide of potassium; but if a mixture of hydrated oxide of chromium, with a solution of potash and an excess of hydrocyanic acid, be exposed to the air, the liquid acquires a reddish brown colour, and a chromicyanide of potassium is formed (Beckmann), corresponding to the ferricyanides and cobalticyanides. These salts are of small importance, and have been but little examined: the *chromicyanide of potassium* (K_3,Cr_2Cy_6) forms brownish red anhydrous prisms; its solution precipitates nitrate of silver, white; salts of cobalt, blue; and the protosalts of iron, of a brick-red: but it gives no precipitate with persalts of iron, or with nitrate of lead.

6 and 7. OSMIO-CYANIDES and RUTHENIO-CYANIDES may, according to Claus, be obtained, corresponding in composition to the ferrocyanides, which they greatly resemble in the colour of the precipitates they form when mixed with salts of copper, iron, zinc, and lead.

(1398) 8. PLATINO-CYANIDES.—Gmelin ascertained that platinum is capable of entering into combination with cyanogen, and forming a series of double cyanides, which are amongst the most beautiful substances which are known: these compounds are analogous to the foregoing, but their composition differs from that of any of the preceding series: for example, the following formulæ represent a few of the platino-cyanides:—

Hydroplatino-cyanic acid . . .	$H,PtCy_2$.
Platino-cyanide of potassium . .	$K,PtCy_2+3\,Aq$.
Platino-cyanide of cuprammonium	$(CuH_3,N),PtCy_2+Aq$.

Platino-cyanide of Potassium is best formed by dissolving protochloride of platinum in a solution of cyanide of potassium; but it may also be obtained by fusing ferrocyanide of potassium with spongy platinum; or by heating a concentrated solution of bichloride of platinum with an excess of cyanide of potassium. This beautiful salt forms long transparent rhombic prisms, which are yellow by transmitted, and blue by reflected light: it is very soluble in water, and more sparingly so in alcohol and in ether. *Platino-cyanide of magnesium* is a beautiful salt which crystallizes in rosettes from its solution in a mixture of alcohol and ether: these crystals form square prisms, which are of a rich crimson by transmitted light, and green or blue by reflected light; they are very soluble in water, and the solution is colourless.* The most characteristic tests of the platino-cyanides are the formation of a beautiful smalt-blue precipitate when a platino-cyanide is added to a solution of subnitrate of mercury in excess, and a flocculent blue precipitate with the salts of copper.

(1399) There is another very beautiful series of salts, commonly termed the *Platinic-cyanides*, which crystallize in prisms of a coppery lustre when viewed by reflected light, but they appear green by transmitted light, and polarize light powerfully; their solutions, however, are colourless. These salts, when dissolved in water, produce a white precipitate with salts of silver and of red oxide of mercury, a blue with the subsalts of mercury, and a greenish-blue with salts of copper. These salts have been carefully examined by Hadow, who has shown that the usually received formula ($M_2Pt_2Cy_5$) is erroneous, and that they are more complicated in construction. The salt commonly known as platinic-cyanide of potassium is really a *chloroplatino-cyanide* ($K_6Pt_6Cy_{12}Cl = 5\,KPtCy_2,KPtCy_2Cl$); but salts exist which correspond in appearance with this, containing either an atom of bromine, or an atom of NO_6, or of SO_4. In order to prepare these compounds in a state of purity, Hadow converts the platino-cyanide of potassium into the colourless perchloroplatino-cyanide ($KPtCy_2Cl$), or into the perbromoplatino-cyanide ($KPtCy_2Br$), by the use of an excess of chlorine or bromine, and crystallizing out the salt. He then mixes the compound so obtained with platino-cyanide in the ratio of 5 atoms of the latter with 1 atom of the former; and, on crystallizing, the copper-coloured compound is obtained in a state of purity. They appear to be double salts of the platino-cyanides with the perchloroplatino-cyanides. The platino-cyanides are, indeed, remarkable for their strong tendency to form double salts. Amongst others a very beautiful double salt of potassium and magnesium ($MgPtCy_2,KPtCy_2+7$ Aq) may be obtained. For further details respecting the platino-cyanides, see Knop, Liebig's *Annal.* xliii. 111; Quadrat, *ib.* lxiii. 164, and lxx. 300; and Hadow, *Q. J. Chem. Soc.* xiii. 106.

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* The changes of colour which this salt experiences by change in its condition of hydration are very remarkable (Hadow). The ordinary red salt ($Mg,PtCy_2 + 7\,Aq$) when gently warmed, even under water, becomes yellow, and if crystallized at 160°, yellow crystals with 6 Aq are deposited. At 212° the salt still retains 2 Aq when it is white, and between 300° and 400° it becomes anhydrous, and is then yellow. These singular changes of colour may be strikingly displayed by allowing a strong solution of the salt to evaporate on a sheet of white paper. When dry, a crimson surface is obtained, but a drop of water upon any point destroys the colour at that spot instantly; on drying, it again reappears. When heated, the red salt first becomes yellow; as the temperature rises it is rendered white; and by a somewhat stronger heat it again becomes yellow. By breathing on the paper, the salt resumes the water that it had lost, the yellow spot becoming successively white, yellow, and eventually crimson.

9 and 10. RHODI-CYANIDES and IRIDI-CYANIDES.—Both rhodium and iridium yield double cyanides analogous to the ferricyanides, but the rhodi-cyanide of potassium is decomposed by acetic acid, with separation of the insoluble cyanide of rhodium. This reaction may be employed in the separation of rhodium from iridium, since acetic acid does not decompose the iridium salt.

(1400) The *iridi-cyanide of potassium* ($K_3Ir_2Cy_6$) forms colourless crystals, and is characterized by giving a deep indigo precipitate with the persalts of iron.

It appears from the foregoing statements, that cyanogen has a strong tendency to produce with several of the metals, electro-negative compounds, which form with hydrogen a series of well-marked acids. The number of atoms of metal, which are united with the cyanogen to constitute the radicles of these acids, varies with the nature of the metal; three different classes of these hydro-acids are known, the first class being monobasic, the second dibasic, and the third tribasic; the composition of their salts with potassium is exhibited as follows:—

1. Monobasic:	Platino-cyanide . .	$K,PtCy_2$
2. Dibasic	Ferro-cyanide . . .	K_2FeCy_3+3 Aq
	Ruthenio-cyanide . .	K_2RuCy_3+3 Aq
	Osmio-cyanide . . .	K_2OsCy_3+3 Aq
3. Tribasic	Ferri-cyanide . . .	$K_3Fe_2Cy_6$
	Cobalti-cyanide . . .	$K_3Co_2Cy_6$
	Chromi-cyanide . . .	$K_3Cr_2Cy_6$
	Iridi-cyanide . . .	$K_3Ir_2Cy_6$
	Rhodi-cyanide . . .	$K_3Ro_2Cy_6$.

(1401) SULPHOCYANIDES.—When cyanide of potassium is fused with sulphur, or even when a solution of the cyanide is boiled with flowers of sulphur, the two bodies enter into com-n, and a new compound (K,CyS_2) is formed: this compound readily prepared by calcining in a covered crucible at a dull at an intimate mixture of 3 parts of anhydrous ferrocyanide ssium, 2 of flowers of sulphur, and 1 part of carbonate of . The melted mass when cold must be treated with boiling and the filtered liquid evaporated; on cooling, striated tic crystals of sulphocyanide of potassium will be deposited: t may be obtained pure by recrystallization from alcohol. operation cyanide of potassium is first formed, whilst c iron is separated; the latter is converted partially into e of iron, and the cyanide of potassium into sulphocyanide, is separated from the iron by solution in water.

lphocyanide of Potassium ($K,CyS_2=97$) is anhydrous but liquescent. It resembles nitre in appearance and in taste; ot poisonous. Boiling alcohol dissolves it abundantly: it n the application of heat. This salt is commonly supposed tain a particular monobasic radicle to which the name of *cyanogen* ($CyS_2=Scy$) has been given. The radicle is, r, not known in a separate condition, but it forms an acid und with hydrogen, and yields numerous well-marked salts. chemists prefer to regard the sulphocyanides as representa- f the cyanates, in which the oxygen of the latter salts has place supplied by sulphur; and the decomposition of hydro- cyanic acid by the aid of heat and acids resembles that of acid under similar circumstances:—

$$2\,\overbrace{(H,C_2NS_2)}^{\text{Hydrosulphocy. acid.}}+2\,H_2O_2=C_2O_4+C_2S_4+2\,H_3N;$$

$$2\,\overbrace{(H,C_2NO_2}^{\text{Cyanic acid.}}+(2\,H_2O_2=C_2O_4+C_2O_4+2\,H_3N.$$

cyanide of ammonium would then correspond to a sulphu- urea, as cyanate of ammonia does to ordinary urea. The ng table represents both views:—

sulphocyanic acid . . .	HS,CyS	H,Scy
cyanide of potassium . .	KS,CyS	K,Scy
cyanide of sodium . . .	NaS,CyS	Na,Scy
cyanide of ammonium . .	H_4NS,CyS	H_4N,Scy
cyanide of calcium . . .	$CaS,CyS+3\,HO$	$Ca,Scy+3\,Aq$
cyanide of copper . . .	CuS,CyS	Cu,Scy
hocyanide of copper . .	Cu_2S,CyS	Cu_2,Scy
cyanide of lead	PbS,CyS	Pb,Scy
cyanide of silver and of po- um	$AgS,CyS+KS,CyS$	$Ag,Scy+K,Scy$
cyanide of mercury and of sium	$HgS,CyS+KS,CyS$	$Hg,Scy+K,Scy$
hocyanide of mercury . .	Hg_2S,CyS	Hg_2,Scy

The view which admits the existence of sul
salt-radicle of these compounds is the one
adopted, and since it renders a simple and sat
the metamorphoses to which the sulphocyanid
be made use of here.

The sulphocyanides of *sodium* and of *a*
drous and deliquescent. Small quantities o
exist in the saliva of man and of the sheep
the sulphocyanides are soluble both in wat
their most characteristic property is the prod
blood-red colour when their solutions are mix
persalts of iron: if the red liquid thus formed
hydrochloric acid, and fragments of zinc be
hydrogen is disengaged, and the colour disap
phocyanide of iron does not form crystals.
lead is sparingly soluble; it is slowly deposite
drous crystals when solutions of acetate of lea
of potassium are mixed. Subacetate of lead giv
with the soluble sulphocyanides. The sulpho
white precipitate (Cu_2CyS_2) when added to a m
of iron with a salt of copper: with the salts o
of suboxide of mercury, they produce white pr

(1402) *Hydrosulphocyanic acid* ($HCyS_2$).–
phocyanide of mercury (Hg_2CyS_2) is decomp
a current of sulphuretted hydrogen, subsulp
produced, and a colourless oily liquid is for
hydrosulphocyanic acid. This acid crystalli
mass at 10°. It boils and may be distilled
is pungent and resembles that of acetic acid.
poison and has a strongly acid taste. In its
soon undergoes decomposition into hydrocyan
persulphocyanic acid ($H_2Cy_2S_6$), since 3 ($HCyS$

Hydrosulphocyanic acid may be obtained in
ing the sulphocyanide of copper, of mercury, o
and decomposing it by means of a current of s
gen. When its diluted solutions are boiled, it
decomposition, ammonia, bisulphide of carbo
being formed. If it be in a more concentrate
into hydrocyanic and hydropersulphocyanic acid
occur more quickly in the presence of other a

Solutions of hydrosulphocyanic acid, and of
are decomposed by the action of nitric acid, and
yellow precipitate being occasioned, which was

sulphocyanogen (CyS_2); the composition of this precipitate, ver, is not known with certainty, but it has been found to in hydrogen as well as sulphur and cyanogen : it is soluble in ation of potash. When this substance is exposed to a strong in a retort, it gives off bisulphide of carbon and sulphur, and ange yellow residue is left, consisting of carbon and nitrogen : this residue bears a dull red heat without decomposition, and itutes Liebig's *crude mellon*, $C_{18}N_{13}$; but if the temperature be d still further it is converted into a mixture of 3 volumes of gen and 1 volume of nitrogen.

f a saturated solution of sulphocyanide of potassium be mixed 8 or 10 times its weight of concentrated hydrochloric acid, it composed, hydrocyanic acid is evolved, and the solution mes semi-solid from the separation of *hydropersulphocyanic* (H_2,Cy_2S_6) in crystalline needles. These crystals are sparingly ble even in boiling water, and as the solution cools it deposits acid in beautiful orange-coloured needles.

(1403) *Mellon* ($C_{18}N_{13}$; Liebig).—This anomalous compound originally supposed by Liebig to contain C_6N_4, but he has ently repeated and varied his experiments upon it, and has ered its formula as above. Mellon is not known in an isolated m in a state of purity, but it constitutes the principal portion the solid residue obtained by heating the yellow precipitate asioned by chlorine in solutions of the sulphocyanides. Mellon ears to be a tribasic radicle, which forms with hydrogen an termed *hydromellonic* acid ($H_3,C_{18}N_{13}$); this latter is an table compound which yields three salts with potassium; a tral mellonide, $K_3,C_{18}N_{13}+10Aq$; a soluble acid mellonide, K_2H, $N_{13}+6$ Aq ; and an insoluble acid mellonide, $KH_2,C_{18}N_{13}$. The tral mellonide is usually formed as a secondary product during preparation of sulphocyanide of potassium; but it is more tifully obtained by fusing 3 parts of pure sulphocyanide of ssium, and gradually adding about one part of crude mellon; very soluble in hot water, from which it crystallizes on cooling 10 Aq. Its solution has an intensely bitter taste. A solu- of mellonide of potassium produces white insoluble mellonides mixed with solutions of nitrate of silver, of corrosive sub- te, and of acetate of lead.

When mellonide of potassium is boiled with an excess of sh it is decomposed, and a new tribasic acid, the *cyameluric* ($O,C_{12}N_7O_3$) is formed: various other compounds are also ined by its decomposition; for details regarding which the er is referred to Liebig's paper (Liebig's *Annal.* xcv. 257).

(1404) *Melam.*—When sulphocyanide of ammonium is submitted to distillation it undergoes decomposition, and yields a mixture of bisulphide of carbon, sulphuretted hydrogen, and ammonia, whilst there remains in the retort a grey insoluble residue, which Liebig has called *melam* ($C_{12}H_9N_{11}$, Liebig; or $C_6H_6N_6$, Gerhardt; calculating from Voelckel's analysis):—

$$8\,\overbrace{(H_4N,C_2NS_2)}^{\text{Sulphocyan. ammon.}} = 2\,C_2S_4 + 4\,H_2S_2 + 5\,H_3N + \overbrace{C_{12}H_9N_{11}}^{\text{Melam.}}.$$

The same substance may be procured by heating an intimate mixture of equal parts of sulphocyanide of potassium and sal-ammoniac. In this process chloride of potassium and sulphocyanide of ammonium are formed, and the sulphocyanide is decomposed by the high temperature, as before, leaving melam, from which the chloride of potassium may be removed by washing.

Melam is a greyish-white granular powder, insoluble in cold water, and in alcohol and ether. Boiling water dissolves it sparingly, and deposits it in the form of a white voluminous powder. When boiled with a solution of potash it is dissolved, and a series of compounds are formed, all of which are closely related. The first of these bodies has been called *melamine* ($C_6H_6N_6$). It is possessed of basic powers, and is deposited in brilliant, colourless, rhombic octohedra; it forms crystallizable salts. A solution of melamine precipitates the oxides of zinc, of iron, of manganese, and of copper from their salts; with nitrate of silver it gives a white crystalline precipitate ($AgO,C_6H_6N_6,NO_5$). Melamine is polymeric with cyanamide (1410). If the mother liquid from which the melamine has been deposited be neutralized with acetic acid, a voluminous white precipitate of *ammeline* ($C_6H_5N_5O_2$) is produced: this substance is a feeble base, which forms a crystallizable salt with nitric acid.

When melamine or ammeline is dissolved in strong sulphuric acid, or when melam is treated with hot nitric acid, and the solution is diluted with twice its bulk of water, and then with alcohol, a white powder termed *ammelid* ($C_{12}H_9N_9O_6$) is precipitated. It is insoluble in water, but is easily soluble, by the aid of heat, in solutions of potash and of ammonia. When either melam, melamine, ammeline, or ammelid is dissolved in concentrated sulphuric acid, and maintained at a temperature just short of boiling for two or three days, until on dilution it ceases to give a precipitate when neutralized with ammonia, it undergoes a change, in consequence of which the elements of ammonia are removed, and those of water are assimilated; and on evaporating the liquid, *cyanuric acid* ($3\,HO,C_6N_3O_3$) is obtained in crystals. In fact, melamine, ammeline, and ammelid may be viewed as amidated derivatives of cyanuric acid, although they have not as yet been obtained directly by acting upon the compounds of cyanuric acid with ammonia. Two other bodies of acid character, viz., the melanuric* and cyameluric acids, also belong to the same group, as may be seen by the following equations, which illustrate the relations of composition which they all bear to cyanuric acid, and the successive stages by which they are produced :—

$$\overbrace{C_6H_6N_6}^{\text{Melamine.}} + H_2O_2 = H_3N + \overbrace{C_6H_5N_5O_2}^{\text{Ammeline.}};$$

$$\overbrace{C_6H_5N_5O_2}^{\text{Ammeline.}} + H_2O_2 = H_3N + \overbrace{C_6H_4N_4O_4}^{\text{Melanuric acid.}};$$

$$\overbrace{C_6H_4N_4O_4}^{\text{Melanuric acid.}} + H_2O_2 = H_3N + \overbrace{C_6H_3N_3O_6}^{\text{Cyanuric acid.}};$$

$$\overbrace{C_{12}H_{12}N_{12}}^{\text{2 Mols. melamine.}} + 3\,H_2O_2 = 3\,H_3N + \overbrace{C_{12}H_9N_9O_6}^{\text{Ammelid.}};$$

$$\overbrace{C_{12}H_9N_9O_6}^{\text{Ammelid.}} = 2\,H_3N + \overbrace{C_{12}H_3N_7O_6}^{\text{Cyameluric acid.}}.$$

The formation of melamine and of ammeline from melam is readily explained, since

$$\overbrace{C_{12}H_9N_{11}}^{\text{Melam.}} + H_2O_2 = \overbrace{C_6H_6N_6}^{\text{Melamine.}} + \overbrace{C_6H_5N_5O_2}^{\text{Ammeline.}}.$$

(1405) *Cyanuric Acid* ($3\ HO,C_6N_3O_3+4\ Aq$).—This polymeride of cyanic acid may be obtained in various ways. 1. By the action of sulphuric acid upon melam or its derivatives, as just described. 2. By the action of a current of dry chlorine upon fused urea; sal-ammoniac, nitrogen, and hydrochloric acid, are thus produced, and cyanuric acid is formed in abundance, $6\,C_2H_4N_2O_2 + 3\,Cl_2 = N_2 + 2\,HCl + 4\,H_4NCl + 2\,(3\,HO,C_6N_3O_3)$: the sal-ammoniac may be removed by washing with cold water, and the cyanuric acid may be crystallized from boiling water. 3. By decomposing hydrochlorate of urea by heat: if the compound formed by transmitting dry hydrochloric acid gas over powdered urea be heated to 293° in an oil bath, rapid decomposition occurs, sal-ammoniac is sublimed, and pure cyanuric acid may be obtained by crystallizing the residue from boiling water; $3\,(C_2H_4N_2O_2,HCl) = 3\,H_4NCl + 3\,HO,C_6N_3O_3$. 4. By heating urea beyond its fusing point until it has become converted into a dry greyish mass, resembling ammelid in appearance and properties: when this residue, which consists of melanuric acid ($C_6H_4N_4O_4$), is dissolved in hot oil of vitriol, to which a small quantity of nitric acid has been added for the purpose of removing the colour, it combines with the elements of water, and at the same time ammonia and cyanuric acid are formed; for $C_6H_4N_4O_4 + H_2O_2 = H_3N + 3\ HO,C_6N_3O_3$: the cyanuric acid is deposited on diluting the liquid moderately with water. 5. By the destructive distillation of uric acid; cyanuric acid being one of the products obtained in this operation. 6. By decomposing solid chloride of cyanogen by prolonged boiling with water, or by dissolving the solid chloride in hydrated alcohol: in the latter case the liquid becomes hot, emits hydrochloric acid, and slowly deposits cyanuric acid in cubes:—

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* Melanuric acid is obtained by heating urea beyond its point of fusion; $4\,C_2H_4N_2O_2 = C_6H_4N_4O_4 + 4\,H_3N + C_2O_4$.

$$C_6N_3Cl_3 + 3\ H_2O_2 = 3\ HCl + 3\ HO,C_6N_3O_3.$$

Cyanuric acid is deposited from its aqueous solution in colourless rhombic prisms, which are efflorescent. It is sparingly soluble in cold water, more freely so in boiling water, and is also somewhat soluble in boiling alcohol. When crystallized from hot hydrochloric or nitric acid, it is deposited in square-based anhydrous octohedra. By long boiling with the concentrated acids it is decomposed into carbonic acid and ammonia. When crystallized cyanuric acid is distilled, it is converted into hydrated cyanic acid, and this hydrate in a few minutes begins to undergo a spontaneous change into the white insoluble compound known as *cyamelid* (411), while the temperature rises spontaneously, owing to the solidification of the mass.

Cyanuric acid is generally considered to be tribasic;* its salts with lead and with silver contain 3 equivalents of a metallic oxide. Most of the cyanurates are sparingly soluble in water. Those of the alkalies and of the alkaline earths contain only two equivalents of fixed base. An acid cyanurate of *ammonia* ($H_4NO, 2\ HO,C_6N_3O_3 + 2\ Aq$) may be obtained in brilliant efflorescent prisms; and an acid cyanurate of *potash* ($KO, 2\ HO,C_6N_3O_3$) is deposited in anhydrous cubes, when acetic acid is added in small quantities at a time to a solution of cyanate of potash, three equivalents of cyanic acid coalescing to form one equivalent of the polymeric cyanuric acid:—

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* Wöhler, however, regards cyanuric acid as dibasic, and considers that 1 atom of water enters into the composition of the acid. (Liebig's *Annal.* lxii. 241.)

$$3\overbrace{(KO,C_2NO)}^{\text{Cyanate of potash.}}+2\overbrace{(HO,C_4H_3O_3)}^{\text{Acetic acid.}}=2\overbrace{(KO,C_4H_3O_3)}^{\text{Acetate of potash.}}+\overbrace{KO,2\,HO,C_6N_3O_3}^{\text{Acid cyanurate of potash.}}.$$

When a solution of a salt of copper, after being saturated with ammonia, is mixed with a solution of cyanuric acid, a characteristic violet precipitate, which is insoluble in cold water, is formed. Cyanurate of *silver* ($3\,AgO,C_6N_3O_3$) is white, and insoluble in water, but soluble in dilute nitric acid. A cyanurate of silver, $2\,AgO,HO,C_6N_3O_3$, may also be obtained.

(1406) *Isomerides of Cyanuric Acid.*—Sometimes during the preparation of cyanuric acid, by boiling crude mellon (1402) with nitric acid, crystals of an acid isomeric with the cyanuric are formed. It crystallizes in long oblique rhomboidal prisms, which are efflorescent: it resembles cyanuric acid, but is distinguished from the latter by its greater solubility; Liebig terms it *cyanilic acid.*

(1407) *Fulminic Acid.*—This remarkable body has not hitherto been isolated in the hydrated form. When a solution of silver or of mercury in an excess of nitric acid is heated with alcohol, a decomposition attended with a copious evolution of gas occurs, and a crystalline deposit of a metallic fulminate is formed.

Fulminic acid is generally assumed to be dibasic, but its power of saturating bases differs from that of dibasic acids in general. Fulminates may be obtained with 2 atoms of a metallic base; or with 1 atom of metallic base, and 1 atom of water, in which latter case the compound has an acid reaction. The 2 atoms of base may consist of 2 atoms of the same easily reducible metallic oxide, or they may consist of two different oxides of reducible metals; for example, fulminates containing 2 atoms of oxide of silver, 2 atoms of oxide of mercury, 2 of oxide of copper, may be obtained, or double fulminates of copper and mercury, or mercury and silver, may be procured; double fulminates of any of these metals with the alkalies, or alkaline earths may also be obtained, but no fulminates with 2 atoms of the alkalies or of the earths are known. If fulminate of silver or of mercury be mixed with a solution of potash in excess, one half only of the silver or mercury is precipitated in the form of oxide, leaving a double fulminate of the alkali and silver, or alkali and mercury in solution.

Fulminate of Silver ($2\,AgO,C_4N_2O_2=2\,AgO,C_2(NO_2)\,C_2N$).—In order to prepare this salt 1 part of silver is dissolved at a gentle heat in 10 parts of nitric acid of sp. gr. 1·36, and the solution poured into 20 parts of alcohol of sp. gr. 0·840. On the application of a very gentle heat, an appearance of ebullition commences, the liquid becomes turbid, *and on cooling* deposits the crystallized fulminate,

which may be washed with cold water,
During the preparation of the salt, v
with fumes of nitrous acid, and of al
formic acids are liberated, and the
oxalic acid.

Fulminate of silver may also
vapours of nitrous acid into an al
silver. In this case crystals of the f
any disengagement of gas in the r
lowing equation :—

$$2\,\overbrace{\mathrm{NO_3}}^{\text{Nitrous acid.}}+\overbrace{\mathrm{C_4H_5O,HO}}^{\text{Alcohol.}}=2\,\overbrace{\mathrm{H}}^{\text{Fu}}$$

Fulminate of silver is sparing
soluble in 36 parts of boiling wate
perty is its extremely explosive natu
or even the slightest friction betwee
to cause its decomposition, attende
ordinary violence. Even when mo
with a hard body will often produce
of a drop of oil of vitriol, or an eleva
over 260° also causes its explosio
chlorine likewise determines its expl
effervescence by dilute sulphuric or
ammonia being formed and hydroc
hydrochloric acid also decomposes
chlorinated acid, the silver being p
of chloride. Sulphuretted hydrogen
of silver and liberates cyanic acid
hydrogen be in excess, is converted i

Solutions of the alkaline chlor
excess, precipitate only one half of
chloride, producing double salts, su
silver and potassium ($\mathrm{AgO,KO,C_4N_2O}$
parts of boiling water. It is a hig
crystallizes in elongated brilliant leaf

An *acid fulminate of silver* (H
tained in the form of a white powde
nitric acid to one of these double fu
boiling water, and crystallizes on co
of mercury it dissolves the oxide, for
silver and mercury.

If a solution of fulminate of s

, or copper, the whole of the silver is precipitated, and a e of mercury or of copper is formed.

ninate of Mercury ($2\ HgO,C_4N_2O_2$) ; *Sp. gr.* 4·4018.—The thod of preparing this salt, according to Liebig, consists lving 3 parts of mercury in 36 of nitric acid, of sp. gr. thout the aid of heat, in a flask capable of containing 18 e bulk of the acid. The solution is then to be poured rge vessel containing 17 parts of alcohol, of sp. gr. 0·830, rediately to be retransferred to the flask which is still full us vapours, and with which it is to be agitated to effect sorption. In a few minutes an effervescence commences, becomes extremely violent, attended with a deposit of mercury, which is gradually redissolved. The reaction moderated by the gradual addition of 17 parts more of and, on cooling, crystals of the fulminate, amounting to s, are deposited. The reaction is attended with the formathe same products as when silver is used. Glycolic acid is nd in the mother liquor.

minate of mercury forms white silky needles, which metallic sweetish taste. It is sparingly soluble in cold but much more soluble in boiling water, and in solution nonia. It may be handled without much danger whilst but if when dry it be exposed to the electric spark, or if it ted to about 360° it explodes; and if it be struck by a dy, or touched with concentrated sulphuric or with nitric tonation occurs, but the suddenness of the explosion is ly less than that of the fulminate of silver. The priming ordinary percussion cap consists of a mixture of 1 part of te of mercury with 6 parts of nitre, or of a mixture of 3 the fulminate, 5 of chlorate of potash, 1 of sulphur, and 1 nd glass. It is applied in the form of a dry powder, and to adhere to the cap by the subsequent application of a shell-lac varnish.

en either zinc or copper is boiled with fulminate of suspended in water, the whole of the mercury is disby the metal which is employed, and fulminate of zinc, or er, is formed.*

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nitrogen in the fulminates appears to be in two different condice these compounds when decomposed yield products containing and cyanogen; fulminate of mercury, for example, when decomboiling it with a solution of hydrosulphate of sulphide of barium, he following compounds:—

$$\overbrace{{}_2(NO_4)Cy}^{\text{mercury.}}+2\overbrace{(BaS,HS)}^{\text{Hydrosulph. bar.}}+H_2O_2=2\ HgS+\overbrace{H_4NCyS_2}^{\text{Sulphocy. ammon.}}+2\ \overbrace{BaO,C_2O_4}^{\text{Carb. baryta.}}$$

(1408) *Fulminuric* or *Isocyanuric acid* ($HO,C_6N_3H_2O$ is an acid which was discovered at about the same time b and by Schischkoff.* Hydrated fulminuric acid cont same elements as the hydrated cyanuric, but it is a m acid, the elements of 2 equivalents of water being uni those of cyanogen and with oxygen to form the acid salts of fulminuric acid are obtained by boiling one of th nates, such as fulminate of mercury, with a solution of o soluble chlorides. When fulminate of mercury is thus bo chloride of potassium, it is gradually dissolved, and a yell pound containing mercury is separated: during the first the operation, the liquid appears turbid, but as soon as pearance ceases it is filtered, and on being evaporated brilliant crystals of fulminurate of potash. The general the reaction may be thus represented (Kekulé):—

$$\overbrace{2\,C_2(NO_4)CyH_2}^{\text{Fulminic acid.}}+H_2O_2=C_2\overbrace{(NO_4)Cy_2H_3O_2}^{\text{Isocyanuric acid.}}+C_2O_4+H_3N$$

In short, the elements of 2 atoms of fulminic acid bec up into 1 atom of fulminuric acid, 1 of carbonic acid, ammonia. The fulminurates crystallize with great facili possess a high lustre and exert a great dispersive power they are decomposed by heat with a feeble explosion.

It thus appears (supposing fulminic acid to be ca existing in the form of a hydrate) that not less than 6 co polymeric with cyanuric acid might be produced, viz.:—

Cyanuric acid . .	$C_6H_3N_3O_6$	=	3	HO,C_6N_3
Cyanilic acid . .	$C_6H_3N_3O_6$	=	3	HO,C_6N_3
Fulminuric acid .	$C_6H_3N_3O_6$	=		HO,C_6H_2
Fulminic acid . .	$C_4H_2N_2O_4$	=	2	HO,C_4N_2
Cyanic acid . .	C_2HNO_2	=		HO,C_2N
Cyamelid . . .	C_2HNO_2	=		HN,C_2O_2

It is a remarkable peculiarity of cyanogen both when when in combination, that it exhibits a strong tendency new compounds by condensation; thus paracyanogen i by the condensation of several molecules of cyanogen into more complex molecule; in like manner the liquid a chlorides of cyanogen are produced by the condensation o molecules of the gaseous chloride into one, and the mol cyanuric acid may be obtained by the condensation of 3 m of cyanic acid into one complex molecule.

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* The latter chemist has rendered it probable that both fulmini cyanuric acids are compounds containing one of the oxides of nitro

409) The action of ammonia upon the oxygen acids of cyano-
has not been fully studied: the group of bodies derived
melam appears to be intimately related to the amides of
ric acid, and would well repay further investigation. The
unds of cyanic acid with ammonia are still more interesting,
they include the remarkable substance known as urea. This
nce has the composition of cyanate of ammonia, and it is
produced when a solution of cyanate of ammonia is evapo-
True cyanate of ammonia may be obtained by transmitting
pour of hydrated cyanic acid into gaseous ammonia, when it
densed in the form of a white voluminous crystalline powder,
is very soluble in water. This solution, when freshly pre-
, disengages ammonia on the addition of potash; but if kept
few days, or if the solution be evaporated at a gentle heat, it
erted into urea.

Urea, however, on account of the important relation which it
to some of the most interesting chemical changes which
within the living body, will be better considered (1411) in
ion with other substances by which it is usually accompanied
e animal organization.

(1410) *Cyanamide* ($C_2H_2N_2$).—Before quitting the subject of
ompounds of cyanogen, mention may be made of the true
of cyanic acid. The most convenient method of pre-
it consists in transmitting a current of gaseous chloride of
gen into ether saturated with ammonia; the muriate of
nia which is deposited during the process, having been sepa-
by filtration, pure cyanamide is left on evaporating the
al solution. It forms a white crystallizable substance,
is soluble without alteration in alcohol. Water dissolves
mide freely, but the residue obtained on evaporating the liquid
d to consist almost wholly of its polymeride melamine (1404).
mide fuses at 104°, and if heated to 300°, it suddenly becomes
with a considerable evolution of heat, and is converted into
ine. The addition of nitric acid to an ethereal solution of
mide, converts it into nitrate of urea; each atom of cyanamide,
assimilation of water in the proportion of H_2O_2, becoming
ed into urea; $C_2H_2N_2+H_2O_2=C_2H_4N_2O_2$.

§ II. BASES OF ANIMAL ORIGIN.

the present section the following compounds and some of
tives *will be described* :—

Urea	$C_2H_4N_2O_2$
Kreatine	$C_8H_9N_3O_4$
Kreatinine	$C_8H_7N_3O_2$
Sarkosine	$C_6H_7NO_4$
Methyluramine	$C_4H_7N_3$
Guanine	$C_{10}H_5N_5O$
Xanthine	$C_{10}H_4N_4O$
Hypoxanthine	$C_{10}H_4N_4O$
Guanidine	$C_2H_5N_3$
Glycocine	$C_4H_5NO_4$
Alanine*	$C_6H_7NO_4$
Leucine	$C_{12}H_{13}N$
Tyrosine	$C_{18}H_{11}N$

(1411) Urea ($C_2H_4N_2O_2=60$).—This important com an essential constituent of the urine of animals; it is abu that of the mammalia, and particularly so in the urine of nivora; but it has also been met with in the urine of bird amphibia. Urea is the principal outlet for the nitroge system, after the materials which compose the animal tis experienced oxidation under the influence of the respir healthy human adult excreting about an ounce of ur Dumas made many fruitless attempts to effect the direct c of the azotised constituents of the body into urea; but states that he has succeeded in obtaining this result jecting albumen to the oxidizing action of permang potash. The correctness of this observation has since be by Stædeler, who obtained benzoic acid abundantly by I method, and which he thinks must have been mistaken Urea is not formed in the kidneys; these glands appear somewhat in the manner of filters, by means of which th separated from the mass of the blood, in which it exist formed before reaching the kidneys.

Urea may be obtained artificially in a variety of of the most remarkable of which was discovered by who showed that a solution of cyanate of ammonia, isomeric with urea, when evaporated at a gentle heat, which:—

$$\overbrace{H_4NO,C_2NO}^{\text{Cyanate of ammonia.}} = \overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

This conversion of the cyanate into urea occurs whe ed by the direct union of hydrated cyanic acid with am- ia, or by the double decomposition of a metallic cyanate, as cyanate of potash, with a salt of ammonia. Neither ic acid nor ammonia can, however, be discovered in the com- nd obtained; but if a solution containing a mixture of nitrate lver and urea be boiled for some time, it is partly resolved into ate of silver and nitrate of ammonia.

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* Alanine is not an animal product, but is described here homology with glycocine and leucine.

Urea is likewise formed during the action of peroxide of lead other oxidizing agents upon uric acid; by the action of lies upon alloxan, and upon kreatine; as well as by the action lphuretted hydrogen upon the double fulminate of copper and onia. It is also obtained as a product of the action of oxy- ide of carbon upon ammonia, and by the re-action of onia upon carbonic ether, at a temperature of 360°. (1010; son.) Urea is metameric with carbamide, if not identical it (1414).

reparation.—1. Urea is readily procured by concentrating to the consistence of syrup, decanting from the deposited and adding an equal bulk of pure colourless nitric acid, of r. 1·25. The mixture becomes nearly solid from the depo- of flaky crystals of nitrate of urea, the quantity of which is ased by immersing the vessel in a frigorific mixture. The er liquor is then pressed out, and the crystals diffused gh water, to which carbonate of baryta in powder has been d. Effervescence takes place from the expulsion of carbonic nitrate of baryta is formed, whilst urea is set free, and is lved. If the mixture of nitrate of baryta and urea, obtained vaporation, be treated with boiling alcohol, urea only is dis- d, and it is deposited on cooling or during evaporation in long, ler, striated, colourless prisms. When an aqueous solution of containing not less than one-thirtieth of its weight of urea is led with an equal bulk of pure nitric acid, an abundant depo- of needles of the nitrate of urea occurs ($C_2H_4N_2O_2,HO,NO_5$). nitric acid employed must be quite free from nitrous acid, since is completely decomposed by nitrous acid, into carbonic acid, gen, and water :—

$$C_2H_4N_2O_2+2\,NO_3=C_2O_4+2\,N_2+2\,H_2O_2.$$

. Oxalic acid may be substituted for the nitric in the fore- process; the oxalate of urea thus formed may be decomposed rbonate of lime, and the urea may then be separated from alate and carbonate of lime by water; on evaporating the us solution, crystals of urea are obtained.

3. Urea, however, is more easily and abundantly obtai
cyanate of potash, procured by heating an intimate mixt
parts of ferrocyanide of potassium, which has been complet
at 212°, with 28 parts of carefully dried finely powdered bl
of manganese. The mixture is placed upon a plate of sheet
heated to dull redness, when it slowly smoulders, care bei
to stir the mass from time to time. The residue of this
when cold is to be digested in cold water, and 41 par
sulphate of ammonia are to be added to the solution
decomposition then ensues, cyanate of ammonia, and su
potash being formed: the cyanate of ammonia may be dis
means of alcohol; it thus becomes converted into ure
crystallizes as the solution cools. Red lead may be substi
peroxide of manganese in the foregoing process: the pr
then being 15 parts of red lead, 8 of the dried ferrocyani
of carbonate of potash. 8 parts of sulphate of ammo
be employed to decompose the solution of cyanate
obtained.

Properties.—Pure urea is colourless; it crystallizes i
striated prisms, which are slightly deliquescent. Its sol
a cooling bitterish taste, and is neutral to test papers.
soluble in water and in hot alcohol, but very sparingly so
It forms no definite compound with water, but it depri
salts, such as sulphate of soda, of their water of crys
when triturated with them, producing a soft semi-flui
Urea melts at about 248°, but at a temperature a li
this it is decomposed, yielding ammonia with cyanate
bonate of ammonia, cyanuric acid being left in the retor
the temperature be raised further, in its turn unde
composition, and a white amorphous residue, consisting of
acid, is obtained:—

$$\overbrace{4\,C_2H_4N_2O_2}^{\text{Urea.}} = \overbrace{C_6H_4N_4O_4}^{\text{Melanuric acid.}} + C_2O_4 + 4\,H_3N.$$

Previously to the completion of this change, a substan
biuret ($C_4H_5N_3O_4 + 2\,Aq$) is formed (1416). By a stil
elevation of temperature melanuric acid is decomposed a
is formed.

A solution of urea, if pure, may be kept at ordinary
tures without alteration, and it may even be boiled witho
going decomposition; but if heated in a sealed tube
284°, each molecule of urea combines with 4 atoms of
is converted into carbonate of ammonia:—

$$\overbrace{C_2H_4N_2O_2}^{\text{Urea.}} + 2\ H_2O_2 = \overbrace{2\ H_4NO,C_2O_4}^{\text{Carb. ammonia.}}.$$

The same change takes place slowly at ordinary temperatures in the presence of the mucus of the bladder, the ammoniacal odour acquired by urine after keeping it for a few days being due to this alteration. A similar decomposition into carbonic acid and ammonia occurs when urea is fused with hydrate of potash, or treated with concentrated sulphuric acid.

Chlorine, when transmitted into an aqueous solution of urea, resolves the latter into carbonic acid and nitrogen, whilst hydrochloric acid is formed:—

$$C_2H_4N_2O_2 + H_2O_2 + 3\ Cl_2 = C_2O_4 + N_2 + 6\ HCl.$$

Urea does not possess well-marked basic properties, but it combines with certain acids, and yields crystallizable compounds, which preserve a strongly acid reaction. It absorbs hydrochloric acid gas, forming a deliquescent substance ($C_2H_4N_2O_2,HCl$) which fuses at a gentle heat to a yellowish oil, and solidifies to a crystalline radiated mass as it cools; water decomposes it immediately. The most important salts of urea are those which it forms with nitric and oxalic acids. In combining with the oxyacids, urea unites with 1 equivalent of acid and 1 of water. *Nitrate of urea* ($C_2H_4N_2O_2,HO,NO_5$) is a compound which crystallizes in rhombic prisms, or in brilliant leaflets which are sparingly soluble in water, especially if it contain excess of nitric acid. It is sparingly soluble in alcohol. *Oxalate of urea* [$2\ C_2H_4N_2O_2,2\ HO,C_4O_6$] crystallizes in long, thin, transparent, sparingly soluble prisms. It is almost insoluble in a saturated aqueous solution of oxalic acid.

(1412) *Compounds of Urea with Salts, and with Metallic Oxides.*—Urea forms definite compounds with certain metallic oxides, such as those of silver and of mercury. Its compound with silver ($3\ AgO,C_2H_4N_2O_2$) is produced by digesting at a gentle heat freshly precipitated oxide of silver in an excess of a solution of urea; a grey or yellowish crystalline powder is thus formed. Three such compounds may be obtained with red oxide of mercury, viz., $C_2H_4N_2O_2,2\ HgO$; $C_2H_4N_2O_2,3\ HgO$; and $C_2H_4N_2O_2,4\ HgO$. The first of these compounds ($C_2H_4N_2O_2,2\ HgO$) is formed, if successive portions of red oxide of mercury suspended in water be mixed with a warm solution of urea; at first the oxide of mercury is completely dissolved, but the compound in question is gradually deposited as a white powder, which becomes yellowish on drying. The compound ($C_2H_4N_2O_2,3\ HgO$) is obtained by adding to a solution of urea rendered alkaline by potash, a solution of corrosive sublimate, taking care to maintain an excess of alkali; a white gelatinous precipitate is formed, which when well washed is converted by boiling water into a pale yellow granular powder, having the composition above indicated; and the compound ($C_2H_4N_2O_2,4\ HgO$) is obtained by precipitating a solution of nitrate of the red oxide of mercury by adding it to an alkaline solution of urea. (Liebig, *Chem. Gaz.*, xii. 41.)

When a solution of the nitrate of red oxide of mercury (mercuric nitrate) is mixed with one of urea, the urea enters into combination with the salt in several proportions. If warm dilute solutions of urea and of the mercurial nitrate be mixed, a crystalline precipitate ($4\ HgO,NO_5,C_2H_4N_2O_2$) falls as a heavy granular powder, which consists of concentric groups of minute needles. But if a dilute solution of the nitrate of mercury be added to a solution of urea so long as a precipitate is formed, and the whole be maintained at a temperature of from 104° to 122° F., the precipitate is principally composed of six-sided prisms, consisting of ($3\ HgO,NO_5,C_2H_4N_2O_2$). If a solution of nitrate of urea be poured into a somewhat dilute solution of nitrate of mercury, slightly acidulated with nitric acid, until a permanent turbidity appears, on filtering the liquid and allowing it to stand, crystalline crusts of small shining rectangular tables are gradually formed ($2\ HgO,NO_5,C_2H_4N_2O_2$).

Nitrate of silver forms two similar compounds, ($AgO,NO_5,C_2H_4N_2O_2$) and [$2\ (AgO,NO_5),C_2H_4N_2O_2$], which crystallize readily when a mixture of a solution of urea and of nitrate of silver is evaporated *in vacuo* over sulphuric acid. Urea also combines with other salts, but the compounds which it forms with them are of little importance.

(1413) *Liebig's method of determining Chlorides and Urea in Urine.*—The foregoing observations are due to Liebig, who has founded upon them a method of determining the quantity of chlorine and of urea in urine, which is valuable when such analyses are numerous, since it enables a large number of comparative experiments to be made in a short time.

1. *For the Chlorine.*—A solution of urea is not precipitated by a solution of corrosive sublimate, but it is immediately precipitated by the nitrate of the red oxide of mercury. Solutions of the chlorides of the metals belonging to the first two groups (439), when mixed with nitrate of mercury, become decomposed into corrosive sublimate, and a nitrate of the alkaline or earthy base; hence, when a solution of chloride of sodium is

mixed with one of urea, no precipitate is occasioned in this liquid on the addition of nitrate of mercury, until the whole of the chloride of sodium has been decomposed by the mercurial salt; $NaCl + HgO,NO_5$ becoming $NaO,NO_5 + HgCl$. After this point has been reached, every fresh addition of the mercurial nitrate occasions a precipitate of the compound $(4\ HgO,NO_5C_2H_4N_2O_2)$; and if a solution of the mercurial salt of known strength and free from excess of acid be prepared, it is easy to determine the quantity of chlorides present by measuring the volume of this solution which it is necessary to add to a given volume of urine before it begins to occasion a precipitate.

2. *For the Urea.*—Having ascertained the number of divisions of the mercurial solution which are consumed before a precipitate begins to be formed, a measured volume of a standard solution of nitrate of silver, sufficient exactly to effect precipitation of the chlorine thus indicated, is added, and afterwards the urea is determined by means of the solution of nitrate of mercury. The following are the details of the operation:—

1. *Preparation of the Solution of Nitrate of Mercury No. 1, employed for determining the Chlorine.*—Crystals of pure subnitrate of mercury are to be dissolved in moderately strong nitric acid, and the solution is to be heated until a sample is no longer rendered turbid by chloride of sodium. The solution is next to be evaporated on a water-bath to a syrupy consistence, and diluted with about ten times its bulk of water and neutralized by the addition of precipitated yellow oxide of mercury as long as it is dissolved; it is then set aside for twenty-four hours, and, if necessary, filtered. In order to graduate the solution, it is necessary to procure a saturated solution of pure chloride of sodium, prepared by digesting a large excess of the salt in cold water, with frequent agitation, for twenty-four hours: 100 water grain measures of such a solution contain 31·84 grains of chloride of sodium. 150 grain measures of this solution (=to 47·76 grains of chloride of sodium) are poured into a small beaker, and mixed with 45 grains of a solution of urea, containing about 4 per cent. of urea, and also with 75 grains of a cold saturated solution of pure sulphate of soda; the solution of nitrate of mercury is then to be added to this mixture from a burette, with constant stirring, until a distinct precipitate is permanently formed. The number of divisions of the solution poured from the burette indicates the amount of the liquid which corresponds to 47·76 grains of chloride of sodium. The strength of the mercurial solution having been thus ascertained, such a proportion of water must be added to it, that 100

water grain measures may correspond to 1 grain of chlo sodium.

2. *Preparation of the Solution of Nitrate of Silver e for removing the Chlorine.*—174·36 grains of fused nitrate are dissolved in water, and diluted until the liquid amounts grain measures; 100 grain measures of this solution corre 1 grain of chloride of sodium.

3. *Preparation of the Solution of Nitrate of Mercury N determining the Urea.*—A concentrated solution of nitrate cury, containing about 25 grains of the salt in 180 grain m is prepared according to the directions already given. to graduate this solution, 60 grains of pure urea are to be diss water, and diluted till the volume of the solution amounts t 3000 grains: 150 grain measures of this liquid are to be pou a beaker, and the mercurial solution is to be added from a till a few drops in a watch-glass produce a distinct yello with carbonate of soda. If the solution were of the exact desired, it would require 300 grain measures of the mercur tion; but if the latter be prepared of the strength above di somewhat smaller quantity will be requisite, and a quantity exactly sufficient to reduce it to this strength must be adde solution.

It will be found convenient, in executing analyses of this method, to be provided, 1. with a pipette capable of d exactly 225 water grains from a mark upon its stem, for ing off the diluted urine; 2. with a small burette divided i measures of water, and capable of measuring 100 gr the mercurial solution No. 1; and 3. with an ordinar meter burette (page 369, Part II.), for the mercurial No. 2.

Before proceeding to determine the amount of th urine, it is necessary to remove the phosphoric acid cont the liquid. This is effected by means of a mixture volumes of cold saturated baryta water, and one volume saturated solution of nitrate of baryta. A glass cylinder one ounce in capacity is filled to overflowing with urine, t being removed by causing a glass plate to slide over the the cylinder; two such cylinderfuls are to be poured into and mixed with one cylinderful of the baryta solution. cipitate thus formed is to be filtered off, and the a chloride of sodium in 225 grain measures of the filtrat grains of urine) is to be determined by *faintly* acidulati addition of nitric acid and then adding the standard s mercury No. 1, till a cloudiness appears: 450 grains more of the filtrate (=300 grains of urine) are then to be measured off into a separate vessel, and mixed with a quantity of the standard solution of silver, equal to twice that of the mercurial solution employed in the preceding experiment. The liquid is to be filtered, and a bulk of the filtrate, equal to 225 measured grains+half the volume of silver solution used, is to be employed for the determination of the urea. This quantity, which corresponds to 150 grains of urine, is to be poured into a beaker, and the graduated mercurial solution No. 2 added from a burette with frequent stirring, until no further increase of the precipitate is perceptible. In order to ascertain whether a sufficient quantity of the mercurial solution has been added, a few drops of the turbid liquid are to be removed with a pipette into a watch-glass, and 2 or 3 drops of a solution of carbonate of soda allowed to flow from the edge of the glass into the liquid. If, after some minutes, the mixture retain its white colour, a further quantity of the mercurial solution is to be added, until a fresh sample plainly exhibits the yellow colour after the addition of the carbonate of soda.

Picard has successfully applied a modification of this method to the detection of urea in healthy blood, and he has even succeeded in estimating the difference in the quantity of urea contained in the blood of the renal artery, and in that of the renal vein after the blood has undergone the depurating influence of the kidney. (*Comptes Rendus*, Sept. 8, 1856.)

(1414) *Compound Ureas.*—A remarkable series of compounds may be obtained from urea by the displacement of a certain number of the atoms of hydrogen which it contains. The formation of these compounds is readily explained upon the hypothesis that urea is the diamide (1171) of carbonic acid: $(C_2O_2)''$ would then occupy the place of H_2 in the double molecule of ammonia; thus urea $C_2H_4N_2O_2 = \left.\begin{matrix}(C_2O_2)'' \\ H_2 \\ H_2\end{matrix}\right\} N_2$, and each of its four atoms of hydrogen would admit of displacement by an equivalent amount of some organic radicle. Compounds of this kind are readily formed in most cases by the action of cyanic acid upon the base which they represent, just as ordinary urea is formed from ammonia, by acting upon it with cyanic acid. They may also be obtained by decomposing the cyanic ethers with ammonia. The compound ureas combine, like ordinary urea, with acids, and form crystallizable salts. Examples of the formation of these compounds have already occurred in the case of the alcohol radicles (1011); thus we have,—

$$\text{Ethyl-urea} \quad = C_6H_8N_2O_2 = \left.\begin{array}{c}(C_2O_2)''\\ C_4H_5\\ H_3\end{array}\right\}N_2,\ \text{or}\ \left.\begin{array}{c}C_4H_7N,\\ HO,CyO\end{array}\right\}$$

$$\text{Ethyl-methyl-urea} \quad = C_8H_{10}N_2O_2 = \left.\begin{array}{c}(C_2O_2)''\\ C_4H_5\\ C_2H_3\\ H_2\end{array}\right\}N_2,\ \text{or}\ \left.\begin{array}{c}C_6H_9N,\\ HO,CyO\end{array}\right\}$$

$$\text{Tetrethyl-urea} \quad = C_{18}H_{20}N_2O_2 = \left.\begin{array}{c}(C_2O_2)''\\ (C_4H_5)_2\\ (C_4H_5)_2\end{array}\right\}N_2,\ \text{or}\ \left.\begin{array}{c}C_{16}H_{20}N,O\\ CyO\end{array}\right\}$$

$$\left.\begin{array}{l}\text{Phenyl-urea}\\ \quad\text{(carbanilamide)}\end{array}\right\} = C_{14}H_8N_2O_2 = \left.\begin{array}{c}(C_2O_2)''\\ C_{12}H_5\\ H_3\end{array}\right\}N_2,\ \text{or}\ \left.\begin{array}{c}C_{12}H_7N,\\ HO,CyO\end{array}\right\}$$

$$\left.\begin{array}{l}\text{Diphenyl-urea}\\ \quad\text{(flavine)}\end{array}\right\} = C_{26}H_{12}N_2O_2 = \left.\begin{array}{c}(C_2O_2)''\\ (C_{12}H_5)_2\\ H_2\end{array}\right\}N_2,$$

$$\text{Phenyl-ethyl-urea} \quad = C_{18}H_{12}N_2O_2 = \left.\begin{array}{c}(C_2O_2)''\\ C_{12}H_5\\ C_4H_5\\ H_2\end{array}\right\}N_2.$$

It is obvious that this class of compounds admits of being multiplied and varied as extensively as the allied group of artificial bases. Some of the natural organic bases, such as nicotylia and conylia, when made to act upon the cyanic ethers, also re-act like ammonia, and give rise to bodies belonging to the class of ureas (1199).

(1415) *Ureides.*—Urea likewise gives rise to the formation of another class of compounds analogous to the amides, forming substances which have been called *ureides*; that is to say, these bodies may be represented as salts of urea from which the elements of water have been abstracted:—

$$\overbrace{H_4N_2C_2O_2,HO,C_{14}H_5O_3}^{\text{Hypothetical benzoate of urea.}} = \overbrace{H_3,C_{14}H_5O_2,N_2C_2}^{\text{Benzureide.}}O_2 + H_2O_2.$$

When, for instance, a mixture of an atom of urea with an atom of one of the oxychlorides of the acids (1094) is heated, decomposition occurs, and a ureide is formed. Thus, if urea be heated to 300°, or 310°, and then gradually mixed with chloride of benzoyl, taking care that the temperature shall not exceed 320°, the mass becomes pasty, the odour of chloride of benzoyl disappears, and benzureide is left in the form of a

line powder, which is soluble in alcohol but insoluble in
—

$$\overbrace{C_{14}H_5O_2Cl}^{\text{Chlor. benzoyl.}}+\overbrace{H_4N_2C_2O_2}^{\text{Urea.}}=\overbrace{H_3,C_{14}H_5O_2,N_2C_2O_2}^{\text{Benzureide.}}+HCl.$$

loride of acetyl, chloride of butyryl, and chloride of valeryl e made in like manner to yield respectively *acetureide* $H_3O_2,N_2C_2O_2]$; *butyrureide* $[H_3,C_8H_7O_2,N_2C_2O_2]$; and *eide* $[H_3,C_{10}H_9O_2,N_2C_2O_2]$. (Zinin.)

sides these ureides, there are various compounds known bear a relation to urea similar to that of the amidated acids nonia:—for example, allophanic acid (1012; $HO,C_4H_3N_2O_5$) e regarded as *carbureic acid*, analogous to carbamic acid: c acid (1436) may in like manner be viewed as *oxalureic* whilst parabanic acid (1435) would represent the imide corling to oxaluric acid (Gerhardt), thus:—

$$\overbrace{HO,H_2NC_2O_3}^{\text{Carbamic acid.}}=\overbrace{H_3N,\quad 2\,HO,C_2O_4}^{\text{Bicarbonate of ammonia.}}-\quad H_2O_2;$$

$$\overbrace{O,C_2H_3N_2O_2,C_2O_3}^{\text{Allophanic acid.}}=\overbrace{C_2H_4N_2O_2,\,2\,HO,C_2O_4}^{\text{Hypothetical carbonate of urea and water.}}-\quad H_2O_2;$$

$$\overbrace{O,C_2H_3N_2O_2,C_4O_5}^{\text{Oxaluric acid.}}=\overbrace{C_2H_4N_2O_2,\,2\,HO,C_4O_6}^{\text{Hypothetical oxalate of urea and water.}}-\quad H_2O_2;$$

$$\overbrace{2\,HO,C_6N_2O_4}^{\text{Parabanic acid.}}=\overbrace{C_2H_4N_2O_2,\,2\,HO,C_4O_6}-2\,H_2O_2.$$

16) *Biuret* ($C_4H_5N_3O_4+2\,Aq$).—This compound has the ition due to bicyanate of ammonia; but it appears to be a derivative from cyanuric acid, and to form one of a series ations of which may be thus represented (Hofmann):—

$$\overbrace{C_6H_3N_3O_6}^{\text{Cyanuric acid.}}+H_2O_2-C_2O_4=\overbrace{C_4H_5N_3O_4}^{\text{Biuret.}};$$

$$\overbrace{C_4H_5N_3O_4}^{\text{Biuret.}}+H_2O_2-C_2O_4=\overbrace{C_2H_7N_3O_2}^{\text{Hydr. oxide guanidine.}};$$

$$\overbrace{C_2H_7N_3O_2}^{\text{Guanidine.}}+H_2O_2-C_2O_4=\overbrace{H_9N_3}^{\text{3 ats. ammonia.}}.$$

with this series runs one derived from cyanuric ether, ndicates the successive stages by which this ether is converted ylia (1012):—

$$\overbrace{C_6(C_4H_5)_3N_3O_6}^{\text{Cyanuric ether.}}+H_2O_2-C_2O_4=\overbrace{C_4H_2(C_4H_5)_3N_3O_4}^{\text{Neutral body.}};$$

$$\overbrace{C_4H_3(C_4H_5)_3N_2O_4}^{\text{Neutral body.}}+H_2O_2-C_2O_4=C_2$$

$$\overbrace{C_2H_4(C_4H_5)_2N_2O_2}^{\text{New base.}}+H_2O_2-C_2O_4=$$

(Hofmann, *Proceed. Roy. Soc.*, xi. 285.)

Biuret is prepared by melting urea for son
at a temperature between 300° and 340°.
ment of ammonia has ceased and the mass
consistence, it is treated with a small quant
and the solution, after filtration, is mixed wi
acetate of lead; cyanuric and melanuric acids
the excess of lead is removed by sulphurett
filtered liquid, on evaporation, yields granul
This compound is very soluble both in wate
may be obtained from its alcoholic solution
foliated crystals. It is a remarkably stabl
may be dissolved by concentrated sulphuric
being decomposed. A characteristic react
formation of an intensely red liquid when a
tion of a salt of copper, followed by the addi
of potash, are added to its aqueous solu
strongly, it is decomposed into ammonia
acid:—

$$\overbrace{3\,C_4H_5N_3O_4}^{\text{Biuret.}}=2\,\overbrace{(3\,HO,C_6N_3O_3)}^{\text{Cyanuric acid.}}$$

(1417) Urea is accompanied in urine
two other crystallizable principles, which ha
of *kreatine* and *kreatinine*. The alkaline pr
extremely feeble. In order to prepare the
the liquid is to be neutralized by lime, and
of calcium added, so long as it produces
filtered liquid is to be evaporated by a water
crystallize on cooling; the mother liquor is
and mixed with one-twentieth of its bulk o
of chloride of zinc. In the course of three
of rounded yellow crystalline grains of chlor
nine, mixed with crystals of kreatine, occu
masses must be washed with cold water,
boiling water, after which hydrated oxide o
till the liquid is distinctly alkaline. The hyd
are thus precipitated from the hot liquid,

of zinc and oxychloride of lead. The filtered solution is
ed with animal charcoal, in order to remove adhering colour-
atter, and, on evaporating the solution, mixed crystals of
ne and kreatinine are deposited. Hot alcohol dissolves the
nine, and during evaporation yields it in crystals. The un-
ed portion is kreatine. If, instead of employing fresh urine
e extraction of kreatine and kreatinine, it be taken after
ction has commenced, the kreatine, according to Liebig,
ave disappeared, whilst the kreatinine remains unchanged.
kreatine and kreatinine were originally discovered among the
uents of the fluids contained in the muscular tissue, whence
erive their name, from κρέας, (flesh.) There can be little
but that, like urea, they are products of disintegration of the
lar tissue, and that they are destined either for ulterior
e in the economy, or for immediate rejection as excrementi-
matter.

reatine ($C_8H_9N_3O_4+2\,Aq=131+18$).—Kreatine is present
juice of the flesh in very small proportion, a pound of flesh
g on an average, according to Gregory, about five grains;
antity, however, varies in the flesh of different animals. The
f the common fowl was found by Gregory to contain more
ne than that of any animal upon which his experiments were
; but cod fish is the cheapest source of kreatine: 10,000
of fresh cod furnish from 9 to 17 parts of kreatine, whilst
me weight of fowl furnishes 32 parts. The best process
ts in chopping up raw cod finely, mixing it with an equal
t of water, and expressing the liquid. This liquid is next
l sufficiently to coagulate the albumen, taking care to avoid
tion, after which it is filtered. Baryta water is then added
usly, so long as it occasions a precipitate; the liquid is again
d, to separate the phosphate of baryta; and the filtrate, on
evaporated to a very small bulk, yields crystals of nearly
kreatine. It may be rendered quite pure by a second crys-
tion.

reatine crystallizes in colourless, transparent, brilliant, ob-
prisms, which, when heated to 212°, become opaque, and
heir water of crystallization. Kreatine is sparingly soluble
d water, of which it requires 75 times its weight for solu-
it is freely dissolved by boiling water. Alcohol, when cold,
ly dissolves it; it is insoluble in ether. The aqueous solu-
as a weak, bitterish taste. Although kreatine is neutral to
apers, it forms definite compounds with some of the acids.
hydrochlorate of kreatine ($C_8H_9N_3O_4,HCl$) forms colourless,

well-defined crystals, which are soluble in water. It may be prepared by mixing solutions of equivalent quantities of hydrochloric acid and kreatine, and evaporating *in vacuo*, or by a temperature not exceeding 90°. The *sulphate* ($2\,C_8H_9N_3O_4,2\,HO,S_2O_6$) may be obtained in a similar manner; the *nitrate* ($C_8H_9N_3O_4,HO,NO$ may also be obtained in brilliant crystals, which have a very sour taste.

When kreatine is boiled with oxide of mercury the oxide is reduced, and a basic substance is formed, which Dessaignes calls methyluramine ($C_4H_7N_3$; 1420). The same substance may be obtained by boiling kreatine with sulphuric acid and peroxide of lead. When a solution of binoxide of nitrogen is transmitted through a solution of nitrate of kreatine, an abundant disengagement of gas occurs; on neutralizing with potash, separating the nitre by crystallization, and adding nitrate of silver, a crystalline compound is obtained (C_6H_5N,AgO,NO_5), composed of nitrate of silver with a new base, to which Dessaignes assigns the formula C_6H_5N.

If kreatine be boiled with either sulphuric, hydrochloric, nitric, or phosphoric acid, it is decomposed, each atom losing 2 atoms of water; whilst kreatinine is formed, and enters into combination with the acid:—

$$\overbrace{C_8H_9N_3O_4}^{\text{Kreatine.}} = \overbrace{C_8H_7N_3O_2}^{\text{Kreatinine.}} + H_2O_2.$$

Alkaline bodies produce with kreatine a different result. If for instance, to a boiling solution of kreatine, crystallized hydrate of baryta, equal in weight to ten times that of the kreatine, be added, the kreatine is gradually decomposed, another new alkali termed *sarkosine* is formed, and urea is found in the liquid; one atom of hydrated kreatine furnishing the elements of one atom of sarkosine and one of urea:—

$$\overbrace{C_8H_9N_3O_4}^{\text{Kreatine.}} + H_2O_2 = \overbrace{C_2H_4N_2O_2}^{\text{Urea.}} + \overbrace{C_6H_7NO_4}^{\text{Sarkosine.}}.$$

By continued boiling with baryta, the urea itself is decomposed into ammonia, which is expelled during the ebullition, and carbonic acid, which combines with the baryta.

(1418) *Kreatinine* ($C_8H_7N_3O_2=113$).—This base may be procured from urine by the method already described (1417). It may also be obtained by boiling kreatine with hydrochloric acid; hydrochlorate of kreatinine is thus formed, and from this the acid may be separated by boiling it with hydrated oxide of lead in excess; a yellow, insoluble oxychloride of lead is formed, and the kreatie remains in solution. Its crystals require about twelve parts cold water for solution, and they are still more soluble in hot ter; kreatinine is also dissolved abundantly by boiling alcohol, l it crystallizes on cooling. Its aqueous solution restores the e colour to reddened litmus, and expels ammonia when heated h solutions of ammoniacal salts. It has a strong tendency to n basic double salts: for example, if a solution of nitrate of er, moderately concentrated, be mixed with one of kreatinine, ecomes converted into a magma of white needles, which are very ble in boiling water; and a similar compound is formed when lution of corrosive sublimate is substituted for that of nitrate ilver. The chloride of zinc and kreatinine ($C_8H_7N_3O_2,ZnCl$) lso sparingly soluble. With the salts of copper, kreatinine s a blue crystallizable compound. Both the sulphate and the rochlorate of kreatinine may readily be obtained in crystals.

(1419) *Sarkosine*, from σὰρξ, flesh ($C_6H_7NO_4=89$).—In order to are this alkali, the solution of kreatine must be boiled with ten es its weight of hydrate of baryta until all odour of ammonia l have disappeared. The excess of baryta is to be removed by rrent of carbonic acid gas; the solution is to be boiled, filtered, evaporated to the consistence of syrup, from which the sarko- e may be obtained in foliated crystals. In order to ensure its rity it may be converted into the form of sulphate, the aqueous tion of which may be decomposed by pure carbonate of baryta. rkosine crystallizes in right rhombic, perfectly transparent, ourless prisms, which are freely soluble in water, sparingly so lcohol, and insoluble in ether. At a temperature a little e 212° they melt, and may be sublimed unchanged. Its ous solution has a sharp, sweetish, somewhat metallic taste, has no action on vegetable colours. It forms crystallizable s, which have an acid reaction. The sulphate ($2\,C_6H_7NO_4, 2\,HO,$ O_3+2 Aq) crystallizes in colourless quadrangular cubes. With hloride of platinum, sarkosine gives a double salt, which by ntaneous evaporation may be obtained in large yellow flattened ohedra ($C_6H_7NO_4,HCl,PtCl_2+2$ Aq). Sarkosine is isomeric h alanine and carbamic ether (urethane), as well as with lacta- e, but quite distinct from all these bodies in properties, and is inguished from them by its insolubility in ether and in alcohol. its reactions Strecker considers it to be *methyl-glycocine*. $C_2H_3)(H_2N)O_4$. (1425)

420) *Methyluramine* ($C_4H_7N_3=73$).—When an aqueous solu- kreatine or of kreatinine is boiled with oxide of mercury, car- acid is *evolved, the oxide is reduced,* and on evaporating the

solution a copious crystallization of oxalate of methyluramine takes place :—

$$\overbrace{2\,C_8H_9N_3O_4}^{\text{Kreatine.}}+5\,Hg_2O_2=\overbrace{2\,C_4H_7N_3,\,2\,HO,C_4O_6}^{\text{Oxalate of methyluramine.}}+2\,C_2O_4+H_2O_2+5\,Hg_2.$$

When the oxalate of the base is decomposed by milk of lime, methyluramine is liberated, and may be obtained in the form of a colourless deliquescent mass, by evaporating the solution *in vacuo.* It is powerfully alkaline, and absorbs carbonic acid rapidly from the air. It has a caustic, somewhat ammoniacal taste. When heated on platinum foil it is almost wholly volatilized. If boiled with baryta water it is decomposed, and vapours of methylia are evolved. Methyluramine, in fact, contains the elements of methylia and of urea minus those of water :—

$$\overbrace{C_4H_7N_3}^{\text{Methyluramine.}}=\overbrace{C_2H_4N_2O_2}^{\text{Urea.}}+\overbrace{C_2H_5N}^{\text{Methylia.}}-H_2O_2.*$$

Oxalate of methyluramine ($2\,C_4H_7N_3,2\,HO,C_4O_6+4\,Aq$) crystallizes in flattened, double prisms, which are very soluble in water. It is easy to prepare other salts of the base, such as the hydrochlorate, the nitrate, and the sulphate, by decomposing the oxalate with a solution containing an equivalent quantity of hydrochlorate, nitrate, or sulphate of lime.

(1421) *Guanine* ($C_{10}H_5N_5O_2=151$) was obtained by Unger from guano; it is also found to constitute the principal portion of the excrement of the garden spider (*Epeira diadema*), and it was found by Scherer in the pancreas of the horse. In order to obtain it from guano, this substance must be boiled with milk of lime until the liquid shall have acquired a yellowish-green tint instead of a brown colour. The liquid must then be filtered, and neutralized with hydrochloric acid. The guanine is slowly deposited, mixed with uric acid, and assumes the form of a flesh-coloured precipitate. This precipitate, when boiled with hydrochloric acid, gives up the guanine, and on cooling, a compound of this body with hydrochloric acid is obtained in crystals : the acid may be removed by digestion with ammonia. Certain specimens of guano were found to yield nearly 6 per cent. of this substance. Guanine forms a yellow powder which is insoluble in water, alcohol, and ether. It appears to possess the properties of a feeble base, and is soluble in dilute acids, forming unstable compounds with them. Gua- e forms both neutral and acid salts, the neutral compound with rochloric acid being [3($C_{10}H_5N_5O_2$,HCl) + 7 Aq], and the acid ($C_{10}H_5N_5O_2$,2 HCl); both of them lose the whole of their acid being heated to 392°. Other salts of guanine contain three ivalents of the base and four of acid. Guanine forms a crys- izable double chloride with bichloride of platinum [($C_{10}H_5N_5O_2$, l),2 $PtCl_2$+4 Aq]. Guanine also combines with the alkalies, is more soluble in alkaline solutions than in the acids. It is ily oxidized by a mixture of chlorate of potash and hydro- ric acid, yielding numerous products, among which are abanic acid, oxaluric acid and urea, the result of the decompo- u of parabanic acid (1435) as well as a new base termed *idine*, by Strecker :—

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* It is worthy of remark, that both kreatine and sarkosine yield methylia when distilled with a mixture of hydrate of soda and lime, and sarkosine, when heated with sulphuric acid, is decomposed with effervescence, emitting vapours of a peculiar, stupifying odour, whilst sulphate of methylia is formed in the liquid.

$$\overbrace{2\,C_{10}H_5N_5O_2}^{\text{Guanine.}}+2\,H_2O_2+3\,O_4=\overbrace{2\,C_6H_2N_2O_6}^{\text{Parabanic acid.}}+2\,C_2O_4+2\,\overbrace{C_2H_5N_3}^{\text{Guanidine.}}.$$

nidine is homologous with methyluramine ($C_4H_7N_3$). It is ably, as Hofmann supposes, a triammonia formed from 3 atoms mmonia, in which 4 atoms of hydrogen have been displaced by carbon C_2,H_5,N_3.

Among the products of the oxidation of guanine is xanthine mall quantity, the formation of which may be represented by following equation :—

$$\overbrace{4\,C_{10}H_5N_5O_2}^{\text{Guanine.}}+3\,O_4=\overbrace{4\,C_{10}H_4N_4O_4}^{\text{Xanthine.}}+2\,H_2O_2+2\,N_2.$$

(1422) *Xanthine* or *Xanthic Oxide* ($C_{10}H_4N_4O_4$) was discovered Marcet as the principal constituent of a very rare variety of uri- y calculus. Göbel has since found it in some oriental bezoars cted from the intestines of certain ruminating animals. The rtions which contain xanthine are of a pale brown colour; y have a polished surface, and a lamellar fracture. These cal- are readily soluble in a solution of potash; and on neutralizing alkaline solution with an acid, xanthine is precipitated in the of a white powder, which is insoluble in water, alcohol, and r. It acquires a waxy lustre on friction with a hard body. caustic alkalies, particularly ammonia, dissolve it freely. drochloric acid dissolves it very sparingly, but it is soluble in cid without effervescence: the solution, when evaporated, lemon-coloured residue (hence the name *xanthine*, from 'yellow'). This residue does not become red by the action nia. When distilled, xanthic oxide yields hydrocyanic *carbonate of ammonia*, but no urea. It contains two atoms of oxygen less than normal uric acid. Stædeler found xanthine diffused pretty extensively through different organs of the body, such as the liver, spleen, and pancreas, as well as the brain and muscular tissue. It may be separated from other bodies with which it is associated by the insolubility of the compound with the red oxide of mercury which is formed on adding acetate of mercury to a solution of xanthine; it also gives a precipitate with subacetate of lead.

(1423) *Hypoxanthine* ($C_{10}H_4N_4O_2$) contains two atoms of oxygen less than the preceding compound. It was found by Scherer in the liquid contained in the substance of the spleen both of man and of the cow. Hypoxanthine has also been found in the thyroid and thymus glands; and it appears to be identical with the base obtained from muscular tissue by Strecker, and called by him *Sarcine.* Hypoxanthine is a white powder, which is nearly insoluble in water, but soluble in a dilute solution of potash, as well as in dilute hydrochloric acid; this acid may indeed be made use of in order to separate the base from xanthine. It is attacked by nitric acid with evolution of gas, and leaves a bright yellow crystalline residue.

Strecker (Liebig's *Annal.* cxviii. 151) has lately pointed out the close relations which exist between several of the bases which have been just described.

Guanine, for example, is regarded by Strecker as a cyanuretted compound triatomic base analogous to cyaniline and to cyanocodeia:—

$$\overbrace{\begin{matrix}(C_2N)_2 \\ \left.\begin{matrix}C_2 \\ (C_4H_2O_2)'' \\ H_3\end{matrix}\right\} N_3\end{matrix}}^{\text{Guanine.}} \qquad ; \qquad \overbrace{\begin{matrix}(C_2N)_2 \\ \left.\begin{matrix}(C_{12}H_5)_2 \\ H_4\end{matrix}\right\} N_2.\end{matrix}}^{\text{Cyaniline.}}$$

If kreatine be the hydrated ammonium base corresponding to kreatinine, we should have the following series:—

$$\overbrace{\left.\begin{matrix}(C_2)^{\text{iv}} \\ (C_4H_2O_2)'' \\ (C_2H_3)H_4\end{matrix}\right\} N_3,O_2}^{\text{Kreatine.}} \; ; \; \overbrace{\left.\begin{matrix}(C_2)^{\text{iv}} \\ (C_4H_2O_2)'' \\ (C_2H_3)H_2\end{matrix}\right\} N_3}^{\text{Kreatinine.}} \; ; \; \overbrace{\left.\begin{matrix}(C_2)^{\text{iv}} \\ C_2H_3 \\ H_4\end{matrix}\right\} N_3}^{\text{Methyluramine.}} \; ; \; \overbrace{\left.\begin{matrix}(C_2)^{\text{iv}} \\ H \\ H_4\end{matrix}\right\} N_3.}^{\text{Guanidine.}}$$

The formula of xanthine would allow of its being considered as forming one of a series homologous with theobromine and caffeine; for

Xanthine . . . . = $C_{10}H_4N_4O_4$
Theobromine . . . . = $C_{14}H_8N_4O_4$
Caffeine . . . . = $C_{16}H_{10}N_4O_4$.

But direct experiments have shown that caffeine is a methyl-derivative of theobromine (1219), and the two bodies stand in a relation similar to that of ethylia to diethylia; whilst as yet the experiments on the conversion of xanthine into theobromine have been unsuccessful; for xanthine when treated with iodide of methyl yields a new methylated base metameric with theobromine, but not identical with it. The formulæ of these bases may probably be thus represented (Strecker):—

$$\overbrace{\left.\begin{array}{l}(C_2N)_2\\(C_2O_2)''\\(C_4H_2O_2)''\\\quad H_2\end{array}\right\}}^{\text{Xanthine.}} N_2;\ \overbrace{\left.\begin{array}{l}(C_2N)_2\\(C_2O_2)''\\(C_4H_2O_2)''\\(C_2H_3)_2\end{array}\right\}}^{\text{Dimethyl xanthine.}} N_2;\ \overbrace{\left.\begin{array}{l}(C_2N)_2\\(C_2O_2)''\\(C_6H_4O_2)''\\\ H,C_2H_3\end{array}\right\}}^{\text{Theobromine.}} N_2;\ \overbrace{\left.\begin{array}{l}(C_2N)_2\\(C_2O_2)''\\(C_6H_4O_2)''\\(C_2H_3)_2\end{array}\right\}}^{\text{Caffeine.}} N_2;$$

xanthine, kreatine and kreatinine, containing *glycolyl* $(C_4H_2O_2)''$ the radicle of glycolic acid, while theobromine and caffeine contain *lactyl* $(C_6H_4O_2)''$, the radicle of lactic acid.

(1424) *Bases homologous with Glycocine.*—The three bases, glycocine, alanine, and leucine, are homologous bodies, and when submitted to the action of nitrous acid they are decomposed according to the following formula, and furnish acids which are also homologous with each other:—

$$(C_{2n}H_{2n+1}NO_4)+(NO_3)_2=(HO,C_{2n}H_{2n-1}O_5)+2\,N_2+H_2O_2.$$

The relation of these bases and acids to each other may be thus represented:—

Bases ($C_{2n}H_{2n+1}NO_4$).		Acids ($HO,C_{2n}H_{2n-1}O_5$).	
Glycocine	$C_4\,H_5\,NO_4$	Glycolic . . .	$HO,C_4\,H_3\,O_5$
Alanine	$C_6\,H_7\,NO_4$	Lactic	$HO,C_6\,H_5\,O_5$
Leucine	$C_{12}H_{13}NO_4$	Leucic	$HO,C_{12}H_{11}O_5$.

The azotised bodies contained in this series possess but very feeble basic power, although they form crystallized compounds with the acids. There can be little doubt that they are the representatives of a class of compounds co-extensive with the volatile fatty acids, and probably the missing terms of the series might be obtained by processes similar to those which furnish alanine and leucine, viz., by acting upon a mixture of hydrocyanic acid with the corresponding aldehyd-ammonia, by means of hydrochloric acid. Glycocine, alanine, and leucine are isomeric with the amides of glycolic, lactic, and leucic acids; but they are not the amides themselves: glycolamide and lactamide may be obtained by acting upon the glycolic and lactic ethers with an alcoholic solution of ammonia, but they differ in properties from glycocine and alanine. Indeed, the true amides are all decomposed into salts of ammonia when boiled with dilute acids, whereas the compounds of the glycocine series may be boiled with dilute acids for hours without decomposition. These bases when submitted to dry distillation yield carbonic acid, and methylia, ethylia, and amylia respectively; for example:—

$$\overbrace{C_4H_5NO_4}^{\text{Glycocine.}} = \overbrace{C_2H_5N}^{\text{Methylia.}} + C_2O_4.$$

(1425) *Glycocine* or *Glycocoll* ($C_4H_5NO_4=75$).—This substance is one of the products of the decomposition of gelatin when boiled with dilute sulphuric acid; after removing the acid by means of carbonate of baryta, the glycocine may be procured in crystals on evaporating the solution. It may also be obtained by heating gelatin with solutions of potash or of soda. But it is most easily obtained in a state of purity by boiling hippuric acid for half an hour, with hydrochloric acid (1252); as the liquid cools, benzoic acid is separated in abundance, and glycocine remains in combination with hydrochloric acid:—

$$\overbrace{HO,C_{18}H_8NO_5}^{\text{Hippuric acid.}}+HCl+H_2O_2=\overbrace{C_4H_5NO_4,HCl}^{\text{Hydrochlor. glycocine.}}+\overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}}$$

On the addition of absolute alcohol, after the solution has been concentrated by evaporation and supersaturated with ammonia, pure glycocine is deposited in minute crystals. Glycocine may also be obtained from glycocholic acid, one of the resinous acids of the bile (1485), when it is decomposed by ebullition with hydrochloric acid. Perkin and Duppa have also obtained glycocine (*Q. J. Chem. Soc.* xi. 31) by acting upon an alcoholic solution of ammonia with bromacetic acid, exposing the mixture to heat in a sealed tube; the reaction is represented as follows:—

$$\overbrace{C_4H_3BrO_4}^{\text{Bromacetic acid.}}+2\,H_3N=\overbrace{C_4H_3O_4,H_2N}^{\text{Glycocine.}}+H_4NBr.$$

Glycocine, in fact, bears the same relation to acetic acid that amido-benzoic does to benzoic acid, and it may therefore be viewed as amido-acetic acid:—

$$\overbrace{HO,C_{14}H_4(H_2N)O_3}^{\text{Amido-benzoic acid.}} \quad ; \quad \overbrace{HO,C_4H_2(H_2N)O}^{\text{Amido-acetic acid.}}$$

$$\overbrace{HO,C_{14}H_5O_3}^{\text{Benzoic acid.}} \quad ; \quad \overbrace{HO,C_4H_3O_3}^{\text{Acetic acid.}}.$$

Pure glycocine has a sweet taste, which is less intense than that of cane-sugar: it is soluble in about 400 parts of cold water, and is less soluble in rectified alcohol; it is insoluble in absolute alcohol and in ether. Glycocine crystallizes readily by sponta-

evaporation of its aqueous solution. It is not susceptible
e alcoholic fermentation. Its solution has the power of red-
g litmus feebly. It throws down metallic mercury from a
ion of the subnitrate of this metal. Glycocine has a strong
ency to combine with the acids, with some of which, such as
sulphuric and hydrochloric, it combines in 2 or 3 different
ortions, without, however, neutralizing them; many of these
ounds, such as the nitrate ($C_4H_5NO_4,HO,NO_5$), crystallize
lly; the sulphate, the oxalate, and the hydrochlorate may
be obtained in crystals. A large number of the metallic
es also combine with glycocine, displacing an equivalent of
er from it, and forming with it soluble compounds, which
y be obtained in crystals; this is the case with the oxides
zinc, of copper, of lead, of barium, and of silver. These
pounds may be obtained by heating the hydrated oxides of the
als with a solution of glycocine. When glycocine is boiled
h acetate of copper, acetic acid is expelled, and a compound of
cocine with oxide of copper is obtained in solution. If glyco-
e be heated with a strong solution of potash it gives a fleeting,
utiful fiery-red colour, ammonia is expelled, and oxalic and
rocyanic acids are formed in the solution. Indeed, few sub-
ces enter so readily into combination as glycocine. In addi-
to its compounds with acids and with bases, it unites with
y salts, and forms bodies which crystallize with great regula-
and brilliancy.

If a mixture of glycocine, with sulphuric acid and peroxide of
ganese or peroxide of lead, be submitted to distillation, a brisk
vescence occurs, owing to the escape of carbonic acid, and
hydrocyanic acid distils over:—

$$C_4H_5NO_4+O_4=C_2O_4+2\ H_2O_2+HC_2N.$$

When nitrous acid is transmitted through an aqueous solution
ycocine, mutual decomposition occurs, nitrogen is disengaged,
on agitating the mixture with ether, decanting the ethereal
d after it has risen to the surface, and submitting it to eva-
ion, glycolic acid (1137) is left in the form of a syrup, which
ely soluble in alcohol:—

$$\overbrace{2C_4H_5NO_4}^{\text{Glycocine.}}+2NO_3=2\overbrace{(HO,C_4H_3O_5)}^{\text{Glycolic acid.}}+H_2O_2+2N_2.$$

6) *Alanine* ($C_6H_7NO_4$).—The interest attaching to this
es from its homologous relation to glycocine, and to its
with *lactic acid.* *It is* isomeric with lactamide, with

sarkosine, and with urethane, but is perfectly distinct from all of them, being in fact *amidopropionic acid* [$HO,C_6H_4(H_2N)O_3$]. Alanine was obtained by Strecker by distilling an aqueous solution containing two parts of aldehyd-ammonia (1077) and one of hydrocyanic acid with an excess of hydrochloric acid. Traces of hydrocyanic and formic acids pass over with the excess of hydrochloric, but no aldehyd. The liquid in the retort is concentrated by evaporation, and a considerable proportion of hydrochlorate of ammonia is separated in crystals. The mother liquor retains hydrochlorate of alanine: it must be boiled with hydrated oxide of lead, which is to be added in small portions to the boiling liquid until it ceases to occasion a disengagement of ammonia. The liquid is then to be decanted from the precipitate, treated with sulphuretted hydrogen to remove the excess of lead, filtered and evaporated. Alanine crystallizes out, and if the mother liquor be mixed with alcohol it furnishes an additional quantity. The reaction by which alanine is formed may be thus represented:—

$$\overbrace{H_3N,C_4H_4O_2}^{\text{Aldehyd ammonia.}}+HC_2N+HCl+H_2O_2=\overbrace{C_6H_7NO_4}^{\text{Alanine.}}+\overbrace{H_4N,Cl.}^{\text{Sal ammoniac.}}$$

Alanine crystallizes in groups of colourless prisms, which are soluble in between 4 and 5 parts of cold water, but are very sparingly soluble in alcohol, and insoluble in ether. Its aqueous solution has a very sweet taste: it is without action upon test-papers. Alanine may be partially sublimed at a temperature a little above 400°. If heated suddenly, it melts and is decomposed, becoming converted into ethylia and carbonic acid: when heated on platinum foil it burns with a violet flame. Hydrate of potash decomposes it, ammonia and hydrogen are disengaged, whilst acetate of potash and cyanide of potassium are obtained. When distilled with dilute sulphuric acid and peroxide of lead, carbonic acid, aldehyd, and ammonia are formed. But its most interesting metamorphosis is that which it undergoes when the aqueous solution is treated with nitrous acid, in which case lactic acid is formed, whilst nitrogen is liberated:—

$$\overbrace{2\ C_6H_7NO_4}^{\text{Alanine.}}+2\,NO_3=\overbrace{2\,(HO,C_6H_5O_5)}^{\text{Lactic acid.}}+H_2O_2+2\,N_2.$$

Alanine, like glycocine, forms numerous compounds both with acids and with bases; many of them may be obtained in crystals, but they are all very soluble.

The compounds ($C_8H_9NO_4$) and ($C_{10}H_{11}NO_4$), intermediate between alanine and leucine, in the glycocine series, and corresponding to the aldehyd ammonias of propionic and butyric acids, have not as yet been prepared, but according to Gorup Besanez, the butyric compound accompanies leucine in the pancreas of the ox.

(1427) *Leucine, Caseous oxide*, or *Aposepedine* ($C_{12}H_{13}NO_4$).—Various decompositions give rise to the formation of this body, which may be viewed as amido-caproic acid [$HO,C_{12}H_{10}(H_2N)O_3$]. It is one of the products of the putrefaction of casein, or of cheese, of muscle, and of gluten, in the presence of water; and it is also amongst the compounds obtained by the action either of sulphuric acid diluted with 3 or 4 parts of water, or of hydrate of potash, upon gelatin, muscular tissue, the yellow elastic tissue of the *ligamentum nuchæ*, white of egg, horn, and wool. One of the best methods of obtaining leucine consists in fusing dried casein or any other albuminoid substance with its own weight of hydrate of potash; during this operation ammonia is evolved, and a disgusting fæcal odour is emitted: as soon as hydrogen begins to come off, which is indicated by the change of colour from dark brown to yellow, the mass must be allowed to cool; and on treating it with hot water, a highly alkaline liquid is obtained, which contains in solution *leucine* and *tyrosine* (Bopp, Liebig's *Annal.* lxix. 21). On slightly supersaturating the liquid with acetic acid, tyrosine is deposited in concentric groups of needles; and on further evaporation of the mother liquid, leucine is obtained in pearly colourless plates, which may be purified by washing them with alcohol, and recrystallizing the residue from boiling dilute alcohol. Limpricht has also succeeded in obtaining leucine artificially, by boiling the compound of valerianic aldehyd and ammonia with an excess of hydrocyanic and hydrochloric acids, until the oily liquid produced by the fusion of the valeraldehyd-ammonia has disappeared: in this manner sal ammoniac and leucine are obtained:—

$$\overbrace{H_3N,C_{10}H_{10}O_2}^{\text{Valeraldehyd ammonia.}}+\overbrace{H,C_2N}^{\text{Hydrocy. acid.}}+HCl+H_2O_2=\overbrace{C_{12}H_{13}NO_4}^{\text{Leucine.}}+\overbrace{H_4N,Cl}^{\text{Sal ammoniac.}}.$$

The excess of hydrochloric acid may be removed by means of oxide of lead, and the traces of lead may be separated by hydrosulphuric acid, after which the liquid is evaporated in a water-bath: boiling dilute alcohol then dissolves leucine from the residue, and deposits it in plates as it cools. Thialdine, when treated with oxide of silver and water, does not yield leucine, as was stated by Gössmann (Hofmann).

Cloetta has made the interesting observation that leucine is one of the normal constituents of the pulmonary tissue; and by operating upon considerable masses of bullocks' lungs he procured it associated with taurin, inosin, and uric acid. It has also been found as a normal constituent of the spleen (Stædeler) and pancreas, and has been obtained from the urine in cases of typhus, and affections of the spinal cord.

Leucine somewhat resembles cholesterin in appearance; it has an unctuous feel, and is lighter than water. When heated cautiously, leucine may be sublimed before it melts, without undergoing decomposition, and may be collected in the form of woolly flocculi. At a higher temperature it becomes brown, and melts at about 340°, and when heated a little beyond this point it furnishes a distillate composed of a yellow oily liquid, containing free carbonate of ammonia, whilst a brown resinous substance remains in the retort. The oily distillate consists chiefly of amylia. Leucine is sparingly soluble in cold water, but freely so in boiling water. The presence of acetic acid or of acetate of potash favours its solution both in water and in alcohol. Cold absolute alcohol dissolves it very sparingly, and it is insoluble in ether. It is, however, easily soluble in dilute solutions of the acids, with many of which it forms crystallizable compounds; the *hydrochlorate* of leucine ($C_{12}H_{13}NO_4,HCl$) is very soluble in water; the *nitrate* of leucine or *nitroleucic acid* ($C_{12}H_{13}NO_4,HO,NO_5$) crystallizes in colourless needles. An aqueous solution of leucine occasions a white precipitate with subacetate of lead; and if to a boiling solution of leucine mixed with the neutral acetate of lead, ammonia be cautiously added, pearly scales ($PbO,C_{12}H_{13}NO_4$) are deposited. Leucine also precipitates subnitrate of mercury (Braconnot) but no other metallic solutions.

Leucine, when distilled with peroxide of lead, furnishes ammonia and butyric aldehyd. If it be distilled with dilute sulphuric acid and peroxide of manganese, valeronitrile with carbonic acid and water are produced:—

$$\overbrace{C_{12}H_{13}NO_4}^{\text{Leucine.}}+O_4=\overbrace{C_{10}H_9N}^{\text{Valeronitrile.}}+C_2O_4+2\,H_2O_2.$$

If a solution of leucine be treated with chlorine in excess, carbonic acid is liberated, and a mixture of valeronitrile and chlorvaleronitrile is obtained, which is separated in the form of volatile oily drops, whilst a quantity of hydrochlorate of leucine is formed in the retort (Schwanert).

If leucine be fused with hydrate of potash it yields valerate and carbonate of potash, whilst ammonia and hydrogen are liberated:—

$$\overbrace{C_{12}H_{13}NO_4}^{\text{Leucine.}}+3\,(KO,HO)=\overbrace{KO,C_{10}H_9O_3}^{\text{Valerate of potash.}}+2\,\overbrace{KO,C_2O_4}^{\text{Carb. potash.}}+H_3N+2\,H_2.$$

Pure leucine is stated also to undergo a similar decomposition when caused to ferment, by the addition of a small quantity of muscular fibre, or of albumen. When an aqueous solution of leucine is submitted to the action of nitrous acid, the leucine is decomposed with liberation of nitrogen and the formation of *leucic acid* ($HO,C_{12}H_{11}O_5$), just as glycolic and lactic acids are formed from glycocine and alanine under similar circumstances.

(1428) *Tyrosine* ($C_{18}H_{11}NO_6$; Hinterberger).—This substance was obtained by Liebig from the products of the fusion of well-dried cheese, fibrin or albumen, with hydrate of potash, in the manner described when treating of the preparation of leucine. The crude crystals of tyrosine must be redissolved in a solution of potash, and precipitated with acetic acid. If coloured it must be converted into hydrochlorate, digested with animal charcoal, and the filtered liquid whilst boiling must be mixed with acetate of potash; chloride of potassium is thus formed, and tyrosine, free from acetic acid, is deposited in long fibrous crystals. Tyrosine is also found among the products of the putrefaction of albumen, fibrin and casein, and it is produced, together with leucine, when these albuminoid bodies are boiled for some hours with dilute sulphuric or hydrochloric acid. Horn, feathers, and hair, also yield it by this treatment:—one part of horn, 4 of oil of vitriol, and 12 of water, if boiled for forty hours, furnish a dark brown fluid, which at the end of that time must be rendered alkaline by the addition of milk of lime, then heated and filtered: sulphuric acid must now be added to neutralization, and on evaporation, crystals of tyrosine will be deposited; they may be purified in the manner already directed.

Tyrosine in certain cases is a direct product of the chemical actions in the living animal; it was found by De La Rue ready formed in the cochineal insect, and has been met with in the pancreas and other internal organs of the higher animals, as well as in the urine in typhus, and in certain spinal affections.

Tyrosine forms long fibrous crystals, which are very sparingly soluble in cold water, and nearly insoluble in alcohol and in ether; boiling water dissolves it in considerable quantity. Although its solutions are neutral to test paper, it is freely soluble both in acid and in alkaline solutions; it combines with 2 atoms of base, forming compounds like that with baryta ($C_{18}H_9Ba_2NO_6 + 4\,Aq$). With sulphuric acid it forms a colligated crystallizable acid ($HO,C_{18}H_{10}NO_5,S_2O_6$); if this be neutralized with lime, and mixed with perchloride of iron, it gives a characteristic violet solution. When treated with hot nitric acid, tyrosine yields oxalic acid; and if cold dilute nitric acid be employed, *nitrate of nitrotyrosine* ($C_{18}H_{10}(NO_4)NO_6,HO,NO_5$) is formed. A very delicate test of the presence of tyrosine is afforded by the formation of a red flocculent precipitate when its solution is heated with a nearly neutral solution of nitrate of the red oxide of mercury, and if the solution be very dilute a rose-red colour is developed in the liquid (R. Hoffman). Tyrosine belongs to a class of compounds not homologous with glycocine, but which, as appears from the researches of Stædeler, present some analogies with it.

§ III. URIC ACID AND ITS DERIVATIVES.

(1429) URIC, OR LITHIC ACID ($C_{10}H_4N_4O_6 = 2\,HO,C_{10}H_2N_4O_4 = 18 + 150$).—This important excrementitious product occurs in small quantity in human urine. It is much more abundantly contained in the white, semi-solid excretions of birds; and, in combination with ammonia it constitutes almost the whole of the excrement of serpents, such as the boa. The beds of guano found in the rainless islands of the Pacific, which are formed of the accumulated excrements of countless generations of sea-fowl, consist chiefly of urate of ammonia, which has undergone decomposition more or less extensive. When uric acid is secreted in excess in man, it is often deposited from the urine in the form of hard crystalline grains, forming what is commonly termed red gravel; or it collects into larger masses which, if retained in the bladder, generally acquire considerable size, and constitute the most usual variety of urinary calculus. In gouty patients also uric acid not unfrequently accumulates around the joints affected: and in combination, principally with soda, forms the white friable concretions often improperly called *chalk stones*.

Uric acid is best prepared from the dried urine of the boa by dissolving 1 part of the powdered mass in from 40 to 50 parts of boiling water, to which an excess of potash is added, sufficient to bring the whole of the acid into solution: during this operation ammonia escapes abundantly. The heat must be continued until the ammoniacal odour has disappeared. The brownish liquid thus procured contains an impure urate of potash, which must be filtered while hot, and decomposed by adding a slight excess of hydrochloric acid. Uric acid is immediately separated in minute white crystals; these must be washed with cold water, dissolved a second time in potash, and once more precipitated by hydrochloric acid; the product, after being thoroughly washed, and then dried, is quite pure. Uric acid crystallizes in rhombic tables, the outlines of which are frequently rounded; but when it is deposited from animal fluids the form of the crystals is often much modified. If a cold saturated solution of urate of potash be decomposed by hydrochloric acid, large crystals of the acid are obtained with 4 Aq. This water is expelled when the acid is heated to 212°.*

Pure uric acid is a white crystalline powder requiring 10,000 parts of cold water for solution, to which, however, it imparts a feebly acid reaction. Uric acid is insoluble in alcohol and in ether, but it is dissolved by concentrated sulphuric acid, and is deposited in a hydrated condition on diluting the solution. The urates of potash and of ammonia are more soluble than the free acid. The acid urates of ammonia, of soda, and of lime are frequent ingredients of urinary calculi; the proportion of the lime salt, however, is always very small. The reaction of uric acid with nitric acid and ammonia is highly characteristic, and it enables the acid to be detected in very minute quantities; the method of proceeding will be described under the head of murexid (1441).

(1430) *Urates.*—Uric acid is dibasic. Its salts have been carefully examined by Bensch (Liebig's *Annal.* liv. 189, and lxv. 181.) All the urates are but sparingly soluble in water; they are much more soluble in alkaline solutions, especially when heated. They are also freely soluble in solutions of borax. Two urates of potash may be formed: the *acid* salt ($KO,HO,C_{10}H_2N_4O_4$) is the one best known. It is precipitated in a granular form when carbonic acid is transmitted through a solution of the neutral salt. It is soluble in about 80 parts of boiling water, from which, on cooling, it is deposited in amorphous flocculi; it requires about 800 parts of cold water for solution. The *neutral urate of potash* ($2\,KO,C_{10}H_2N_4O_4$) is obtained by saturating a cold dilute solution of potash, free from carbonate, with uric acid suspended in water, and boiling down the solution in a retort. At a certain degree of concentration the salt is deposited in fine anhydrous needles: the clear liquid must be decanted from them, and they must be washed with dilute alcohol. This salt requires about 44 parts of cold water for solution, and 35 of boiling water. Its solution is slowly decomposed by ebullition. This salt has a caustic taste, and rapidly absorbs carbonic acid from the air.

There are two *urates of soda*, both of which are anhydrous; they are each somewhat less soluble than the corresponding potash salts. The *acid urate of ammonia* ($H_4NO,HO,C_{10}H_2N_4O_4$) is the only urate of ammonia which is known. It usually forms a white amorphous mass, which is soluble in 1800 parts of cold, and 240 of boiling water; it is deposited in fine needles from a boiling aqueous solution of it, which contains an excess of ammonia. *Urate of lithia* is more soluble than any other of these salts. Hence lithia water is occasionally prescribed to gouty patients, and to others who suffer from a superabundance of uric acid. Only the *acid urate of magnesia* ($MgO,HO,C_{10}H_2N_4O_4 + 6\,Aq$) is known; but both a neutral ($2\,CaO,C_{10}H_2N_4O_4$) and an acid urate of *lime* ($CaO,HO,C_{10}H_2N_4O_4 + 2\,Aq$) may be obtained.

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* When uric acid is long boiled with a solution of potash, 6 equivalents of water are assimilated, and *uroxanate of potash* ($2\,KO,C_{10}H_8N_4O_{10}+6\,Aq$) is formed in small quantity. On the addition of a strong acid, uroxanic acid is separated in sparingly soluble, microscopic, tetrahedral crystals.

(1431) *Products of the Decomposition of Uric Acid.*—When uric acid is submitted to distillation it does not fuse, but undergoes decomposition, producing carbonate of ammonia, hydrocyanic acid, cyanuric acid, urea, and some empyreumatic products. Uric acid is decomposed when heated with fused hydrate of potash, ammonia is evolved, and the residue contains cyanide of potassium mixed with carbonate and oxalate of potash. But the most remarkable chemical peculiarity of uric acid is the facility with which it is altered by oxidizing agents, and the number of definite and crystallizable compounds to which it gives rise. These products were first investigated by Liebig and Wöhler (Liebig's *Annal.* xxvi. 241). Such metamorphoses of animal products by oxidation always present a high degree of interest physiologically considered, inasmuch as the great changes which occur under the influence of vitality are changes in which oxidation plays the principal part. The oxidation of uric acid may be effected in various ways, such as by means of nitric acid, by peroxide of lead, by ferricyanide of potassium mixed with caustic potash; the products of oxidation differing according to the nature of the agent employed.

The following table exhibits the most important of the derivatives of uric acid:—

Uric acid	$2\,HO,C_{10}H_2N_4O_4$	$= C_{10}H_4N_4O_6$
Uroxanic acid . . .	$2\,HO,C_{10}H_8N_4O_{10}$	$= C_{10}H_{10}N_4O_{12}$
Alloxan	$C_8H_2N_2O_8 + 2\,Aq$	$= C_8H_2N_2O_8 + 2\,Aq$
Dialuric acid . . .	$HO,C_8H_3N_2O_7$	$= C_8H_4N_2O_8$
Alloxantin	$\left\{\begin{array}{l} C_8H_2N_2O_8 \\ +C_8H_3N_2O_7 + 5\,Aq \end{array}\right\}$	$= C_{16}H_4N_4O_{14} + 6\,Aq$ or $C_8H_2N_2O_7 + 3\,Aq$
Alloxanic acid . .	$2\,HO,C_8H_2N_2O_8$	$= C_8H_4N_2O_{10}$
Mykomelinic acid .	$HO,C_8H_3N_4O_3 + Aq$	$= C_8H_4N_4O_4 + Aq$
Mesoxalic acid . .	$2\,HO,C_6\quad O_8$	$= C_6H_2\quad O_{10}$
Leucoturic acid . .	$HO,C_6H_2N_2O_5$	$= C_6H_3N_2O_6$
Difluan	$C_6H_4N_2O_5$	$= C_6H_4N_2O_5$
Parabanic acid . .	$2\,HO,C_6\quad N_2O_4$	$= C_6H_2N_2O_6$
Oxaluric acid . . .	$HO,C_6H_3N_2O_7$	$= C_6H_4N_2O_8$
Uramil (dialuramide)	$H_2N,C_8H_3N_2O_6$	$= C_8H_5N_3O_6$
Thionuric acid . .	$2\,HO,C_8H_3N_3O_6,S_2O_4$	$= C_8H_5N_3O_{12}S_2$

. . . . .		$= C_{24}H_{12}N_{10}O_{16}$?
. . . . .		$= C_8 H_6 N_4 O_6$
acid . .	$HO,C_8 H_8N_4O_8$	$= C_8 H_9 N_4 O_9$
acid . .	$HO,C_{10}H_6N_2O_8$	$= C_{10}H_7 N_2 O_9$
acid . .	$HO,O_6 H_4N_2O_6$	$= C_6 H_5 N_2 O_7$.

and Wöhler have shown that when uric acid is sub-
he oxidizing action of dilute nitric acid it is converted
nd alloxan :—

$$\overbrace{{}_0H_2N_4O_4)}^{\text{acid.}}+4\,H_2O_2+O_4=2\,\overbrace{(C_8H_2N_2O_8,\,2\,HO}^{\text{Alloxan.}})+2\,\overbrace{C_2H_4N_2O_2}^{\text{Urea.}};$$

xan be boiled with an alkaline solution, it loses the
s nitrogen in the form of urea, whilst mesoxalic acid is

$$\overbrace{C_8H_2N_2O_8,\,2\,HO}^{\text{Alloxan.}}+H_2O_2=\overbrace{C_2H_4N_2O_2}^{\text{Urea.}}+2\,\overbrace{HO,C_6O_8}^{\text{Mesoxalic acid.}}.$$

in these cases decomposed partially or entirely by the
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noxalic acid ($C_8N_2O_4=C_4O_4Cy_2$)—a compound which is
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$$(1)\ \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}}+2\,BaO=2\,\overbrace{BaO,C_8H_2N_2O_8}^{\text{Alloxanate of baryta.}}.$$

potash salts. The *acid urate of ammonia* (H_4NO,HO,C_{10} is the only urate of ammonia which is known. It usual a white amorphous mass, which is soluble in 1800 parts and 240 of boiling water; it is deposited in fine needles boiling aqueous solution of it, which contains an excess monia. *Urate of lithia* is more soluble than any other salts. Hence lithia water is occasionally prescribed t patients, and to others who suffer from a superabundanc acid. Only the *acid urate of magnesia* (MgO,HO,C_1 $+6\,Aq$) is known; but both a neutral ($2\,CaO,C_{10}H_2N_4O_4$ acid urate of *lime* ($CaO,HO,C_{10}H_2N_4O_4+2\,Aq$) may be ol

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Dialuric acid . . .	$HO,C_8H_3N_2O_7$	$=C_8H_4N_2O$
Alloxantin	$\left\{\begin{matrix} C_8H_2N_2O_8 \\ +C_8H_2N_2O_7+5\,Aq \end{matrix}\right\}$	$=C_{16}H_4N_4O$ or $C_8H_5N_2O$
Alloxanic acid . .	$2\,HO,C_8H_2N_2O_8$	$=C_8H_4N_2O$
Mykomelinic acid .	$HO,C_8H_3N_4O_5+Aq$	$=C_8H_4N_4O$
Mesoxalic acid . .	$2\,HO,C_6\quad O_8$	$=C_6H_2\quad O$
Leucoturic acid . .	$HO,C_6H_2N_2O_5$	$=C_6H_3N_2O_6$
Difluan	$C_6H_4N_2O_6$	$=C_6H_4N_2O_6$
Parabanic acid . .	$2\,HO,C_6\quad N_2O_4$	$=C_6H_2N_2O_6$
Oxaluric acid . . .	$HO,C_6H_3N_2O_7$	$=C_6H_4N_2O_8$
Uramil (dialuramide)	$H_2N,C_8H_3N_2O_6$	$=C_8H_5N_3O_6$
Thionuric acid . .	$2\,HO,C_8H_5N_3O_6,S_2O_4$	$=C_8H_7N_3O$

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$$(1)\ \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}}+2\,BaO=2\,\overbrace{BaO,C_8H_2N_2O_8}^{\text{Alloxanate of baryta.}}.$$

$$(2)\ \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}}+\overbrace{H_4NS,HS}^{\text{Hydrosulph. ammonia.}}=\overbrace{H_4NC}^{\text{Dialura}}$$

$$(3)\ \overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}}+\overbrace{HO,C_8H_3N_2O_7}^{\text{Dialuric acid.}}+2$$

$$(4)\ \overbrace{2\,C_8H_2N_2O_8}^{\text{Alloxan.}}+O_4=2\overbrace{(2\,HO,C}^{\text{Parabani}}$$

$$(5)\ \overbrace{2\,HO,C_6N_2O_4}^{\text{Parabanic acid.}}+H_3N+H_2O_2=$$

$$(6)\ \overbrace{HO,C_6H_3N_2O_7}^{\text{Oxaluric acid.}}+H_2O_2=2\,\overbrace{HO,}^{\text{Oxalic}}$$

(1432) *Alloxan* ($C_8H_2N_2O_8+2$ an
adding to nitric acid (of sp. gr. 1·42)
tions at a time, waiting till the ef
addition of each separate quantity has
moderate the heat generated by the rea
in cold water if necessary. The temp
rise much above 120° F. During this
nitrogen escape abundantly. Uric a
tals begin to be formed; the liquid
when an abundant deposit of octohe
occur. These crystals must be drai
structed with asbestos, washed with
a tile. In this form alloxan was re
big and Wöhler, but later research
contains 2 atoms of water, since Gm
to from 300° to 320° it loses 11·3
octohedral crystals be redissolved in
evaporation transparent prisms cont
The changes which attend the format
by the action of nitric acid, may be
secutive stages, though the decompos
taneously :—

$$(1)\ 2\,(\overbrace{2HO,C_{10}H_2N_4O_4}^{\text{Uric acid.}})+H_2O_2+2\,($$

$$2\,\overbrace{C_2H_4N_2O_2}^{\text{Urea.}}+2$$

But, since urea and nitrous acid
other, nitrogen and carbonic acid are
whilst water and ammonia are for
alloxan :—

$$(2)\ \overbrace{2\,C_2H_4N_2O_2}^{\text{Urea.}}+2\,NO_3=2\,C_2$$

Alloxan may also be prepared by mixing 4 parts of uric acid with 8 of commercial hydrochloric acid, and gradually adding 1 part of powdered chlorate of potash. Under these circumstances no effervescence occurs, and the whole of the urea is found in solution. The temperature must be carefully prevented from rising too high.

Alloxan is freely soluble in water; it stains the skin pink, and gives it a sickly odour, and, though not possessed of acid properties, it reddens litmus paper. In its anhydrous condition it is a stable and definite substance; but in its hydrated form it often becomes spontaneously decomposed into parabanic and oxaluric acids. When alloxan is boiled with peroxide of lead it yields urea and carbonic acid, the peroxide of lead being converted into protoxide:—

$$\overbrace{C_8H_2N_2O_8,\ 2\,HO}^{\text{Alloxan.}} + 4\,PbO_2 = \overbrace{C_2H_4N_2O_2}^{\text{Urea.}} + 3\,C_2O_4 + 4\,PbO.$$

A characteristic property of alloxan is the formation of an intensely violet purple-coloured liquid on admixture with solution of a protosalt of iron. Long-continued boiling decomposes a solution of alloxan, carbonic acid is given off, and the solution contains a mixture of parabanic acid and alloxantin:—

$$3\,(\overbrace{C_8H_2N_2O_8,\ 2\,HO}^{\text{Alloxan.}}) = (\overbrace{C_{16}H_4N_4O_{14},\ 6\,HO}^{\text{Alloxantin.}}) + 2\,\overbrace{HO,C_6N_2O_4}^{\text{Parabanic acid.}} + C_2O_4.$$

(1433) *Alloxanic Acid* (2 $HO,C_8H_2N_2O_8$).—By treating alloxan with baryta water, so long as the precipitate produced is redissolved on agitation, and gently heating the mixture, two equivalents of water are displaced by the baryta, and a salt is formed which crystallizes as the liquid cools. This compound contains *alloxanic acid*, which may be separated by the cautious addition of sulphuric acid, and may be obtained in crystals by evaporation.*

A solution of alloxan in ammonia is nearly colourless, but if heated gently it becomes yellow, and on cooling forms a semi-solid

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* Alloxanic acid is an unstable compound. If its aqueous solution be boiled, carbonic acid is emitted; and if the solution be rapidly reduced to the consistence of a syrup, and then diluted with water, it is only partially dissolved; the insoluble portion is named by Schlieper (Liebig's *Annal.* lvi. 1) *leucoturic acid* ($HO,C_6H_2N_2O_5$); the solution contains a white deliquescent body, termed *difluan* ($C_6H_4N_2O_5$). Nitric acid reconverts the latter into alloxan, and potash decomposes it with evolution of ammonia and formation of oxalic acid. The formation of these bodies from alloxanic acid may be thus indicated:—

$$4\,(\overbrace{2\,HO,C_8H_2N_2O_8}^{\text{Alloxanic acid.}}) = 2\,(\overbrace{HO,C_6H_2N_2O_5}^{\text{Leucoturic acid.}}) + 2\,\overbrace{C_6H_4N_2O_5}^{\text{Difluan.}} + 4\,C_2O_4 + H_2O_2.$$

transparent gelatinous mass of *mykomelinate of ammonia*, whilst the liquid retains urea in solution, with alloxanate and mesoxalate of ammonia; these are probably the results of secondary actions. Mykomelinic acid contains the elements of 1 equivalent of alloxan and 2 of ammonia, from which 4 equivalents of water have been separated :—

$$\overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}}+2\,H_3N=\overbrace{HO,C_8H_3N_4O_3}^{\text{Mykomelinic acid.}}+2\,H_2O_2.$$

Hlasiwetz states that when this acid is heated to 360° or 380° with water under pressure, it is dissolved, with evolution of a quantity of gas, whilst mykomelinic acid remains in solution; and he suggests that certain yellow sediments which have been regarded as urate of ammonia may really consist of this acid, which evolves ammonia when heated with potash, and yields murexid when treated with nitric acid (*Liebig's Annal.* ciii. 216) :—

$$2\,\overbrace{HO,C_{10}H_2N_4O_4}^{\text{Uric acid.}}=\overbrace{HO,C_8H_3N_4O_3}^{\text{Mykomelinic acid.}}+\overbrace{C_2O_2}^{\text{Carb. oxide.}}.$$

If alloxanic acid be neutralized by ammonia it gives with nitrate of silver a white precipitate, which, by boiling, first becomes yellow and is converted into mesoxalate of silver, and is afterwards reduced with effervescence.

(1434) *Mesoxalic Acid* ($2\,HO,C_6O_8$).—When alloxanate of baryta is subjected to prolonged boiling it is decomposed; urea is liberated, and a yellowish precipitate is formed, consisting of a mixture of carbonate of baryta and a sparingly soluble mesoxalate of baryta, the carbonate of baryta being the result of a secondary decomposition of the urea. The following equation shows the process of the transformation of alloxanic into mesoxalic acid :—

$$2\,\overbrace{BaO,C_8H_2N_2O_8}^{\text{Alloxanate of baryta.}}+H_2O_2=2\,\overbrace{BaO,C_8O_8}^{\text{Mesoxalate of baryta.}}+\overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

Mesoxalic acid may be procured in a free state by the addition of sulphuric acid to the baryta salt: the solution when evaporated yields crystals, which are very soluble in water; it is powerfully acid, and has a very sour taste. The most characteristic reaction of mesoxalic acid is the formation of a yellow precipitate of mesoxalate of silver, when a solution of mesoxalate of ammonia is mixed with one of nitrate of silver: this precipitate when heated is decomposed with a brisk effervescence, owing to the escape of carbonic acid and carbonic oxide, whilst metallic silver is left; $2\,AgO,C_6O_8=2\,Ag+2\,C_2O_4+C_2O_2$. When to a boiling solution lloxan a boiling solution of acetate of lead is added, a yellow, y, insoluble precipitate of mesoxalate of lead is formed, from ch the acid may be obtained by decomposing the precipitate by us of sulphuretted hydrogen.

(1435) *Parabanic Acid* ($2\ HO,C_6N_2O_4$) is formed by concenting the acid mother liquor of alloxan, till on cooling it forms oft crystalline mass; $C_8H_2N_2O_8+HO,NO_5=2\ HO,C_6N_2O_4+$ O_4+HO,NO_3. This is to be dried on a tile, redissolved in water, recrystallised, when it forms thin, colourless, six-sided prisms: a powerful acid, very permanent in its uncombined condi, and very soluble in water. At a heat of 212° it acquires a dish tint: at a higher temperature it undergoes partial subation, but a portion of it is decomposed, and furnishes hydroic acid. Parabanic acid forms salts which are exceedingly table; parabanate of silver being the only salt which is perent. All the other parabanates during evaporation combine two atoms of water, and become converted into oxalurates: banate of ammonia, for instance, when boiled furnishes brilliant tals of oxalurate of ammonia:—

$$\overbrace{HO,H_4NO,C_6N_2O_4}^{\text{Parabanate of ammonia,}}+H_2O_2=\overbrace{H_4NO,C_6H_3N_2O_7}^{\text{Oxalurate of ammonia,}}.$$

(1436) *Oxaluric Acid* ($HO,C_6H_8N_2O_7$).—This acid is interg from the circumstance of its being occasionally met with in ary sediments, forming the dumb-bell crystals that were at mistaken for oxalate of lime. Oxalurate of ammonia may be yed in preparing the acid; a hot saturated solution of this when mixed with dilute sulphuric acid, and cooled rapidly, pure oxaluric acid as a sparingly soluble heavy white powder. ing boiling with water this acid is decomposed into oxalic acid oxalate of urea:—

$$\overbrace{(HO,C_6H_3N_2O_7)}^{\text{Oxaluric acid.}}+2\ H_2O_2=2\ \overbrace{HO,C_4O_6}^{\text{Oxalic acid.}}+2\ \overbrace{C_2H_4N_2O_2,\ 2\ HO,C_4O_6}^{\text{Oxalate of urea.}}.$$

Oxalurate of silver is a white salt, soluble in hot water, from h it crystallizes in beautiful silky needles as the solution cools. nic and oxaluric acids may be regarded as ureic derivatives acid (1415).

7) *Alloxantin* ($C_8H_2N_2O_7+3\ Aq$) or ($C_{16}H_4N_4O_{14}+6\ Aq$). compound may be regarded as a combination of dialuric alloxan, since it may be formed by mixing solutions of bodies *in equivalent proportions*:—

$$\overbrace{C_8H_2N_2O_8, 2\,HO}^{\text{Alloxan.}}+\overbrace{HO,C_8H_3N_2O_7}^{\text{Dialuric acid.}}+H_2O_2=\overbrace{C_{16}H_4N_4O_{14}, 6\,HO}^{\text{Alloxantin.}};$$

the crystals of alloxantin are slowly deposited from the
ture. Alloxantin may also be obtained by the action o
oxidizing agents upon alloxan. If alloxan be dissolved
water, and a current of sulphuretted hydrogen be transmi
the liquid in a short time becomes turbid, from the
ration of sulphur, and crystals of alloxantin are gradually d
sited. The acid mother liquor which remains after the p
ration of alloxan by nitric acid is well adapted for furnis
alloxantin; it should be neutralized with chalk, and submitt
the action of a current of sulphuretted hydrogen gas. Many
processes may, however, be adopted for preparing alloxantin;
example, if protochloride of tin be mixed with a solutio
alloxan, crystals of alloxantin are deposited. Also, if a sol
of alloxan be acidulated with hydrochloric acid, and a bar of
be introduced, hydrogen is evolved, and crystalline crust
alloxantin are slowly produced.

Alloxantin forms small white, hard, brilliant prismatic cry
which become pink by exposure to an atmosphere conta
ammonia. It is very sparingly dissolved by cold water, but
freely by boiling water; its solution reddens litmus. Crysta
alloxantin may be heated to 212° without losing weight, bu
higher temperature it gives off 15·4 per cent. of water.
water, when added to its solution, gives a characteristic viol
cipitate, which becomes white if boiled in the liquid. A solu
alloxantin reduces the salts of silver, and is converted into al
thus affording an instance of the facility with which oxi
agents reconvert it into alloxan. Hlasiwetz found that
alloxantin is heated under pressure with water, to 360°, or
it is slowly decomposed, evolving gas in large quantity,
oxalate of ammonia is formed, probably owing to the fol
reaction :—

$$\overbrace{C_{16}H_{10}N_4O_{20}}^{\text{Alloxantin.}}+2\,H_2O_2=2\,\overbrace{H_4NO,C_4O_6}^{\text{Oxalate of ammonia.}}+2\,H_3N+2\,\overbrace{C_2O_4}^{\text{Carb. acid.}}+4\,\overbrace{C_2O}^{\text{Carb. oxide.}}$$

If a boiling solution of alloxantin be mixed with a soluti
muriate of ammonia, also at a boiling temperature, and the m
be allowed to cool in a well-corked vessel, crystals of *uram*
luramide) are deposited, whilst the liquid retains alloxan an
hydrochloric acid in solution :—

$$\overbrace{C_{16}H_4N_4O_{14}}^{\text{Alloxantin.}}+H_4NCl=\overbrace{C_8H_5N_3O_6}^{\text{Uramil.}}+HCl+\overbrace{C_8H_2N_2O}^{\text{Alloxan.}}$$

loxan is boiled with hydrochloric acid it is gradually decom- loxan and parabanic acid are formed, accompanied by two ds, termed by Schlieper *allituric* acid ($C_6H_3N_2O_4$) and *dili-* id. The last named acid has not been analysed in its ned form.

8) *Dialuric Acid* ($HO,C_8H_3N_2O_7$).—If a stream of sulphu- drogen be transmitted in excess through a hot solution n or of alloxantin, sulphur is deposited, and the liquid be- rongly acid, owing to the formation of *dialuric acid*. If this id be neutralized with ammonia, dialurate of ammonia is l in silky needles ($H_4NO,C_8H_3N_2O_7$). The same salt may ed by reducing alloxan by means of zinc and hydrochloric l adding a sufficient excess of ammonia to redissolve the zinc, which is at first precipitated by the ammonia. If of ammonia be added to hot hydrochloric acid, so it is dissolved, and the liquid be allowed to cool, long of dialuric acid are deposited. They become red by to the air, and are gradually converted into alloxantin. acid forms a sparingly soluble salt with *potash*. It may ed by adding a solution of cyanide of potassium to one n. The brown yellow precipitate thus obtained must be in a weak potash ley, and neutralized by acetic acid, falls as a white precipitate. The dialurate of *ammonia* is the moment of its formation, but as it dries it becomes ndid pink or blood-red colour. This salt is freely soluble g water. It occasions a white precipitate with the salts , and a yellow one with salts of lead. Nitrate of silver is by it to the metallic state.

9) *Uramil*, or *Dialuramide* ($C_8H_5N_3O_6=H_2N,C_8H_3N_2O_6$). compound may be obtained by decomposing thionurate of by boiling it for a few minutes with an acid:—

$$\overbrace{2\,H_4NO,C_8H_3N_3O_6,S_2O_4}^{\text{Thionurate of ammonia.}}+2\,HCl+H_2O_2=$$

$$2\,H_4NCl+2\,HO,S_2O_6+\overbrace{C_8H_5N_3O_6}^{\text{Uramil.}}.$$

lso be procured by mixing boiling solutions of alloxantin ate of ammonia, freed from air (1437). Uramil crystallizes orm groups of brilliant hard needles, which are insoluble in er, and sparingly soluble even in boiling water. When to an atmosphere containing traces of ammonia it a rose tint. Uramil is freely soluble in dilute alkaline at *ordinary temperatures*, and is deposited from them

$$\overbrace{C_8H_2N_2O_8, 2\,HO}^{\text{Alloxan.}}+\overbrace{HO,C_8H_3N_2O_7}^{\text{Dialuric acid.}}+H_2O_2=\overbrace{C_{16}H_4N_4O_{14}, 6\,HO}^{\text{Alloxantin.}};$$

the crystals of alloxantin are slowly deposited from the mixture. Alloxantin may also be obtained by the action of deoxidizing agents upon alloxan. If alloxan be dissolved in water, and a current of sulphuretted hydrogen be transmitted, the liquid in a short time becomes turbid, from the separation of sulphur, and crystals of alloxantin are gradually deposited. The acid mother liquor which remains after the preparation of alloxan by nitric acid is well adapted for furnishing alloxantin; it should be neutralized with chalk, and submitted to the action of a current of sulphuretted hydrogen gas. Many other processes may, however, be adopted for preparing alloxantin; for example, if protochloride of tin be mixed with a solution of alloxan, crystals of alloxantin are deposited. Also, if a solution of alloxan be acidulated with hydrochloric acid, and a bar of zinc be introduced, hydrogen is evolved, and crystalline crusts of alloxantin are slowly produced.

Alloxantin forms small white, hard, brilliant prismatic crystals, which become pink by exposure to an atmosphere containing ammonia. It is very sparingly dissolved by cold water, but more freely by boiling water; its solution reddens litmus. Crystallized alloxantin may be heated to 212° without losing weight, but at a higher temperature it gives off 15·4 per cent. of water. Baryta water, when added to its solution, gives a characteristic violet precipitate, which becomes white if boiled in the liquid. A solution of alloxantin reduces the salts of silver, and is converted into alloxan; thus affording an instance of the facility with which oxidizing agents reconvert it into alloxan. Hlasiwetz found that when alloxantin is heated under pressure with water, to 360°, or 370°, it is slowly decomposed, evolving gas in large quantity, whilst oxalate of ammonia is formed, probably owing to the following reaction :—

$$\overbrace{C_{16}H_{10}N_4O_{20}}^{\text{Alloxantin.}}+2\,H_2O_2=2\,\overbrace{H_4NO,C_4O_6}^{\text{Oxalate of ammonia.}}+2\,H_3N+2\,\overbrace{C_2O_4}^{\substack{\text{Carb.}\\\text{acid.}}}+4\,\overbrace{C_2O_2}^{\substack{\text{Carb.}\\\text{oxide.}}}.$$

If a boiling solution of alloxantin be mixed with a solution of muriate of ammonia, also at a boiling temperature, and the mixture be allowed to cool in a well-corked vessel, crystals of *uramil* (dialuramide) are deposited, whilst the liquid retains alloxan and free hydrochloric acid in solution :—

$$\overbrace{C_{16}H_4N_4O_{14}}^{\text{Alloxantin.}}+H_4NCl=\overbrace{C_8H_5N_3O_6}^{\text{Uramil.}}+HCl+\overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}}.$$

When alloxan is boiled with hydrochloric acid it is gradually decomposed, alloxan and parabanic acid are formed, accompanied by two compounds, termed by Schlieper *allituric* acid ($C_6H_3N_2O_4$) and *dilituric* acid. The last named acid has not been analysed in its uncombined form.

(1438) *Dialuric Acid* ($HO,C_8H_3N_2O_7$).—If a stream of sulphuretted hydrogen be transmitted in excess through a hot solution of alloxan or of alloxantin, sulphur is deposited, and the liquid becomes strongly acid, owing to the formation of *dialuric acid*. If this acid liquid be neutralized with ammonia, dialurate of ammonia is deposited in silky needles ($H_4NO,C_8H_3N_2O_7$). The same salt may be obtained by reducing alloxan by means of zinc and hydrochloric acid, and adding a sufficient excess of ammonia to redissolve the oxide of zinc, which is at first precipitated by the ammonia. If dialurate of ammonia be added to hot hydrochloric acid, so long as it is dissolved, and the liquid be allowed to cool, long needles of dialuric acid are deposited. They become red by exposure to the air, and are gradually converted into alloxantin. Dialuric acid forms a sparingly soluble salt with *potash*. It may be obtained by adding a solution of cyanide of potassium to one of alloxan. The brown yellow precipitate thus obtained must be dissolved in a weak potash ley, and neutralized by acetic acid, when it falls as a white precipitate. The dialurate of *ammonia* is white at the moment of its formation, but as it dries it becomes of a splendid pink or blood-red colour. This salt is freely soluble in boiling water. It occasions a white precipitate with the salts of baryta, and a yellow one with salts of lead. Nitrate of silver is reduced by it to the metallic state.

(1439) *Uramil*, or *Dialuramide* ($C_8H_5N_3O_6=H_2N,C_8H_3N_2O_6$).—This compound may be obtained by decomposing thionurate of ammonia by boiling it for a few minutes with an acid:—

$$\overbrace{2\,H_4NO,C_8H_3N_3O_6,S_2O_4}^{\text{Thionurate of ammonia.}}+2\,HCl+H_2O_2=$$

$$2\,H_4NCl+2\,HO,S_2O_6+\overbrace{C_8H_5N_3O_6}^{\text{Uramil.}}.$$

It may also be procured by mixing boiling solutions of alloxantin and muriate of ammonia, freed from air (1437). Uramil crystallizes in penniform groups of brilliant hard needles, which are insoluble in cold water, and sparingly soluble even in boiling water. When exposed to an atmosphere containing traces of ammonia it acquires a rose tint. Uramil is freely soluble in dilute alkaline solutions at ordinary temperatures, and is deposited from them unaltered on adding an acid. But if its solution in ammonia be boiled, it gradually acquires a rich purple colour, and on cooling deposits crystals of *murexid* :—

$$H_3N + 3\,\overbrace{C_8H_5N_3O_6}^{\text{Uramil.}} + O_4 = \overbrace{C_{24}H_{12}N_{10}O_{16}}^{\text{Murexid.}} + 3\,H_2O_2.$$

If uramil be boiled for some time with oxide of mercury or of silver a similar change occurs; the metallic oxide is reduced, and if the liquid be filtered while hot, beautiful crystals of pure murexid are deposited. An excess of the metallic oxide must be carefully avoided, otherwise the purple colour disappears, and alloxanate of ammonia is formed in the liquid. A solution of uramil in potash evolves ammonia when heated; at ordinary temperatures it slowly absorbs oxygen from the air, acquiring a fine purple colour, and depositing crystals of purpurate of potash; the liquid becomes neutral, and contains alloxanate and mesoxalate of potash.

(1440) *Thionuric Acid* ($2\,HO,C_8H_3N_3O_6,S_2O_4$).—If an aqueous solution of alloxan be added to a solution of sulphite of ammonia containing a considerable quantity of free ammonia, and the mixture be boiled for a few minutes, the ammonia and sulphurous acid unite with the elements of alloxan. As the liquid cools, a beautiful salt, termed *thionurate of ammonia*, is deposited :—

$$\overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}} + S_2O_4 + 3\,H_3N = \overbrace{2\,H_4NO,C_8H_3N_3O_6,S_2O_4}^{\text{Thionurate of ammonia.}}.$$

By adding a solution of acetate of lead to the solution of this salt, an insoluble gelatinous thionurate of lead is procured, which on standing becomes converted into concentric groups of delicate needles. This precipitate, on being decomposed by sulphuretted hydrogen, gives pure thionuric acid, which may be obtained by evaporation at a gentle heat, crystallized in slender needles. Its aqueous solution may be preserved unchanged at ordinary temperatures, but it undergoes decomposition when boiled; sulphuric acid being formed, whilst silky crystals of uramil are deposited. The thionurate of ammonia gives a pale yellowish brown precipitate with salts of copper. It gives no precipitate in acid solutions with salts of baryta, but a white one in neutral solutions: when mixed with nitrate of silver the metal is gradually reduced, and forms a mirror-like coating on the sides of the vessel which contains it.

(1441) *Murexid*, or *Purpurate of Ammonia* ($C_{24}H_{12}N_{10}O_{16}$?).—There are various modes of forming this beautiful compound.

The decomposition of uramil by ammonia under the influence of oxygen, and by the action of oxide of mercury, have been already mentioned (1439). Another advantageous method of preparing murexid consists in adding alloxan to an ammoniacal solution of uramil. If the formula given for murexid be correct, this reaction must be attended with the absorption of oxygen:—

$$6\,\overbrace{C_8H_5N_3O_6}^{\text{Uramil.}}+10\,H_3N+O_4+6\,\overbrace{C_8H_2N_2O_8}^{\text{Alloxan.}}=4\,\overbrace{C_{24}H_{12}N_{10}O_{16}}^{\text{Murexid.}}+12\,H_2O_2.$$

Murexid may also be obtained by adding a solution of carbonate of ammonia, drop by drop, to a boiling solution of alloxan, until the liquid has a slightly ammoniacal odour; the solution then acquires a beautiful purple tint, becomes turbid, and on cooling deposits 4-sided prismatic crystals of murexid. Murexid may also be prepared on a small scale by dissolving 4 grains of alloxantin with 7 of hydrated alloxan, in half an ounce of boiling water, and mixing the solution whilst hot with 80 grains of a cold saturated solution of carbonate of ammonia; brisk effervescence ensues, and a splendid purple liquid is produced, which on cooling deposits magnificent green crystals of murexid, with a golden lustre. These crystals, when heated to 212°, lose water to the extent of 3 or 4 per cent. Its brilliant colour is speedily destroyed by sulphuretted hydrogen, as well as by free ammonia. Murexid is but sparingly soluble in cold water, to which, however, it communicates its intense purple colour; hot water takes it up more freely.

When the solution of murexid is mixed with salts of lead, of baryta, and of silver, it yields purple precipitates. Corrosive sublimate slowly but completely decolorizes a solution of murexid, giving a beautiful purple precipitate. A solution of acetate of zinc yields a golden yellow precipitate in a solution of murexid, forming a brilliant iridescent film in which green and yellow tints predominate. Dilute acids decompose the crystals of murexid, and cause the separation of scales of a sparingly soluble yellowish substance, termed *murexan*, which, in all probability, is an impure form of uramil; the solution contains a mixture of alloxan and alloxantin.

Murexid is a body resembling an amide in composition. The exact composition of this compound is not accurately established, but the formula above given agrees with the analyses of Liebig and Wöhler. Fritsche, from his experiments, represents its composition by the somewhat improbable formula ($C_{16}H_8N_6O_{11}$), which does not explain the mode of the formation of murexid.

The colouring principle of murexid has lately been applied successfully to the dyeing of silks and cotton, and less perfectly to wool. Silk may be dyed by simple immersion in a concentrated solution of corrosive sublimate mixed with murexid. Cotton goods are mordanted with lead. Nitrate of lead is thickened and mixed with a proportion of murexid sufficient to give the desired shade: it is then printed, the cloth dried and immersed in a bath containing 1 part of corrosive sublimate, 1 of acetate of soda, and 100 of water (Lauth). Dyeing on wool with murexid may be effected if the fabric be first mordanted with 'pink salt,' the double chloride of tin and ammonium.

Test for Uric Acid.—Advantage is taken of the formation of murexid, in order to detect very minute quantities of uric acid by the action of nitric acid. In applying this test, the substance supposed to contain uric acid is heated on a slip of glass with a drop of nitric acid, and evaporated cautiously to dryness. If uric acid be present, the residue has a red colour, which is converted by exposure to the vapour of ammonia into a fine crimson, and the addition of a drop of a solution of potash developes a splendid purple colour, which disappears on the application of heat, with extrication of ammonia.

(1442) *Allantoin* ($C_4H_3N_2O_3$ or $C_8H_6N_4O_6$).—This is a body which occurs in the allantoic fluid of the cow, or in the urine of the fœtal calf, but it may also be procured by the oxidation of uric acid. For this purpose, 1 part of uric acid must be suspended in 20 parts of water, and raised to the boiling point; finely levigated peroxide of lead is then to be added in small quantities at a time to the boiling liquid, until the oxide ceases to change colour. The peroxide of lead is reduced to the state of protoxide, and a brisk effervescence occurs, owing to the escape of carbonic acid, whilst oxalic acid is precipitated in combination with protoxide of lead; the supernatant liquid is colourless, and on filtering it and allowing it to cool, hard, brilliant, prismatic crystals of allantoin are deposited. Upon further concentration of the solution, fresh crystals of allantoin are obtained, and when the mother liquid has been evaporated until it acquires a syrupy consistence, crystals of urea are deposited. The reaction which attends the formation of allantoin is not well understood, and the equations hitherto given do not satisfactorily account for all the products. Liebig and Wöhler consider the reaction to be as follows (doubling the proportions given by these chemists to allow of doubling the molecular formula for allantoin);—

$$\overbrace{HO,C_{10}H_3N_4O_4)}^{\text{Uric acid.}}+4\,PbO_2+3\,H_2O_2=2\,\overbrace{(2\,PbO,C_4O_6)}^{\text{Oxalate of lead.}}$$
$$+\overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}}+2\,\overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

bonic acid arises probably from the oxidizing action of
xide of lead upon the oxalate at the moment of its forma-
Pelouze has however shown that the decomposition is in
nore complicated than it appears to be from the foregoing
.

ntoin is a neutral, tasteless substance, sparingly soluble in
ter, but freely soluble in boiling water. It shows but
ndency to combine with other bodies; but a compound
toin with oxide of silver may be obtained by mixing a
solution of allantoin with one of nitrate of silver, and
mmonia drop by drop; a white precipitate ($C_8H_5AgN_4O_6$)
ccasioned. It is probable, therefore, that the usually re-
rmula of allantoin should be doubled. Allantoin undergoes
tion in the presence of yeast, furnishing urea, oxalate of
a, and an unexamined acid (Wöhler). When allantoin is
ith solutions of the alkalies, it undergoes decomposition,
a being evolved whilst oxalic acid is formed:—

$$\overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}}+H_2O_2+4\,(KO,HO)=4\,H_3N+2\,\overbrace{(2\,KO,C_4O_6)}^{\text{Oxalate of potash.}}.$$

ntoin is readily decomposed by simple elevation of tempe-
when its aqueous solution is heated in a closed tube to
80° it is resolved into a new acid, *allanturic acid* (HO,
O_8; Pelouze), and into carbonate of ammonia; both these
es being produced from the elements of allantoin by the
tion of the elements of water:—

$$\overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}}+6\,H_2O_2=2\,\overbrace{(HO,C_{10}H_6N_4O_8)}^{\text{Allanturic acid.}}+2\,\overbrace{(2\,H_4NO,C_2O_4)}^{\text{Carbonate of ammonia.}}.$$

ntoin also assimilates water and is transformed into allan-
d by heating it gently with nitric acid, or with hydro-
cid, and urea is at the same time formed:—

$$3\,\overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}}+2\,H_2O_2=2\,\overbrace{(HO,C_{10}H_6N_4O_8)}^{\text{Allanturic acid.}}+2\,\overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

uze considers that the urea found in the mother liquor,
during the preparation of allantoin from uric acid by
f peroxide of lead, is due to this secondary action; this,
is very doubtful.

Allanturic acid is a white deliquescent substance, which gives white precipitates with nitrate of silver and with the acetates of lead; these precipitates are soluble in an excess of these salts, as well as in free allanturic acid.

When allantoin is digested for some days with a concentrated solution of potash, then mixed with acetic acid in excess, and treated with a solution of acetate of lead, an insoluble lead salt of a new acid, termed *hidantoic acid* ($HO,C_8H_8N_4O_8$? Schlieper), is formed. The normal acid contains the elements of one equivalent of allantoin with 3 additional equivalents of water. Its anhydride is polymeric with oxamide.

Lantanuric Acid ($HO,C_6H_4N_2O_6$?) is the name given by Schlieper to a result obtained by adding the powdered uric acid to a solution of ferricyanide of potassium and hydrate of potash at ordinary temperatures. Under these circumstances the red prussiate is rapidly converted into the yellow prussiate of potash, whilst nascent oxygen attacks the uric acid; $4\ K_3Fe_2Cy_6 + 4\ (KO,HO) = 8\ (K_2,FeCy_3) + 2\ H_2O_2 + O_4$. Allantoin and carbonic acid are first produced,—

$$\overbrace{2\ (2\ HO,C_{10}H_2N_4O_4)}^{\text{Uric acid.}} + O_4 + 2\ H_2O_2 = 2\ \overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}} + 2\ C_2O_4.$$

and the allantoin combining with an additional quantity of water is resolved into lantanuric acid and urea:—

$$2\ \overbrace{C_8H_6N_4O_6}^{\text{Allantoin.}} + 3\ H_2O_2 = 2\ \overbrace{(HO,C_6H_4N_2O_6)}^{\text{Lantanuric acid.}} + 2\ \overbrace{C_2H_4N_2O_2}^{\text{Urea.}}.$$

It is possible that lantanuric acid may be identical with the allanturic acid of Pelouze: it is a deliquescent substance, which forms a white insoluble salt with oxide of lead, and its properties agree very closely with those ascribed by Pelouze to allanturic acid, respecting the analysis of which no details have hitherto been published.

(1443) Two other substances which have been sometimes found in urine—viz., cystin and kynurenic acid, will be noticed here.

Cystin, or *Cystic Oxide* ($C_6H_6NO_4S_2$).—This substance constitutes a rare form of urinary calculus. Calculi composed of it are semi-transparent and of a brownish-yellow colour, and crystalline texture. Cystin is insoluble in water, alcohol, and ether, but it is dissolved by the stronger acids, such as the sulphuric, nitric, hydrochloric, and phosphoric. It is also freely soluble in alkaline solutions, whether caustic or carbonated, from which it can be precipitated by the addition of an acid such as the acetic. It may readily be obtained crystallized in hexagonal plates by allowing its ammoniacal solution to evaporate spontaneously. When heated it does not melt, but is decomposed, emitting a peculiar fœtid odour. Cystin contains 25·5 per cent. of sulphur.

Kynurenic Acid is the name given by Liebig to a peculiar acid found in the urine of the dog. It forms very light, silky, colourless, delicate needles, which are soluble in alkaline solutions, nearly insoluble in water, and insoluble in alcohol and ether. It is soluble in hot dilute acid solutions, and is deposited from them on cooling. It combines with the alkalies, forming soluble crystalline salts. Kynurenic acid does not appear to contain nitrogen. Its composition has not been ascertained. When heated in a small tube it yields a crystalline sublimate, and leaves scarcely a trace of any carbonaceous residue.

CHAPTER XI.

ALBUMINOID AND GELATIGENOUS PRINCIPLES.

(1444) THE greater number of the compounds of organic origin which have hitherto occupied our attention, are destitute of organic structure; they contain in each of their constituent or equivalent molecules only a moderate number of elementary atoms, in which respect they differ from the compounds which remain to be described, since the latter are of a much more complex character. These bodies enter into the formation of the organized textures, and are destitute of crystalline character. The most important of them—viz., fibrin and albumen, occur both in plants and in animals, and though they form but a small proportion of the solid and liquid components of the organs of plants, they are never entirely wanting in some portion or other of their organism. They are most abundant in the seed. These substances abound, however, in the animal tissues, and constitute their most remarkable and distinctive ingredients. Owing to the complexity of their composition no satisfactory rational formula can at present be assigned to any of these azotised bodies; and, owing to their indisposition to crystallize, great difficulty is experienced in obtaining them in a state of purity, and of ascertaining when they are really free from foreign admixture. All of them contain sulphur amongst their components, though the proportion of this element never exceeds 2 per cent.

These azotised compounds may be subdivided into two groups: of these the more important is termed the *albuminoid* group, owing to the general resemblance of its members to albumen or white of egg; it comprises albumen, fibrin, casein, and legumin, in which the proportion of carbon to nitrogen is that of eight equivalents of the former to one of the latter. The second group is the *gelatigenous:* it comprises gelatin, chondrin, and ossein.

(1445) *Products of Oxidation of the Albuminoid and Gelatigenous Groups.*—When these azotised substances are submitted to the gradual action of oxidizing agents, they furnish a great variety of products, which, however, belong to three principal groups; viz., to the acetic, the benzoic, and the cyanic series. Amongst the volatile bodies furnished by treating albuminoid substances with a mixture of bichromate of potash and sulphuric acid, or with a mixture of peroxide of manganese and sulphuric acid, Guckelberger (*Liebig's Annal.*, lxiv. 39) obtained the following products, besides others which have not been specially identified :—

Formic acid
Acetic acid
Propionic acid
Butyric acid
Valeric acid
Caproic acid

Acetic aldehyd
Propionic aldehyd
Butyric aldehyd.
——

Benzoic acid
Hydride of benzoyl.
——
Hydrocyanic acid
Valeronitrile.

The volatile products of oxidation are the only ones which have as yet been fully examined. The most abundant of these products are the series of volatile acids: next to these the products of the benzoic series occur in the largest quantity, whilst the hydrocyanic is obtained in the smallest quantity. The proportion in which these substances are formed varies according as casein, fibrin, albumen, or gelatin has been the body submitted to oxidation. Gelatin yields the largest quantity of formic, acetic, and valeric acids (Schlieper, *Liebig's Annal.*, lix. 1); fibrin gives the largest proportion of butyric acid, and casein yields the compounds of benzoyl in greatest abundance. There can be no doubt that these bodies originate in more complex organic products, which are the first results of the breaking up of these complicated azotised substances. Thus leucine and tyrosine are amongst the products obtained in an early stage of the reaction, and they break up into valeric acid, ammonia, and probably other compounds. When the albuminoid and gelatigenous substances are fused with hydrate of potash, they yield leucine and tyrosine, together with variable quantities of acetate, rate, and other salts of potash, which belong to the series of y acids.

§ I. The Albuminoid Group.

(1446) It has been already stated that the more important abers of this group are albumen, fibrin, casein, and legumin, it comprises several modifications of these bodies of minor ortance, such as globulin and vitellin. The different forms of tis also exhibit a close relationship to the compounds of this ion.

Albumen is the characteristic ingredient of white of egg, and ie serous portion of the blood. *Fibrin* is the principal constit of muscular tissue, and is that component of the blood h occasions its spontaneous coagulation; *casein* is that conent of milk which is separated in the form of curd on the tion of an acid; it is the essential component of cheese. *umin* is abundant in the seeds of the leguminous plants, such peas, beans, and lentils. Liebig regards legumin as identical h casein; but many other chemists consider that it has hitherto n found only in the vegetable kingdom, and casein only in the mal: albumen and fibrin are, however, generally admitted to ur in both divisions of the organic creation. No animal can tinue to subsist upon food in which these azotised substances entirely wanting. This circumstance is explained by the imant observations of Liebig, who first clearly insisted upon the that none of these proteic principles are ever produced by the nal organism; they are elaborated in the growing plant, and merely assimilated by the animal in the process of digestion. albuminoid principles furnish those essential ingredients of the d which are concerned in repairing the soft azotised portions he body, such as the muscular and nervous tissues, as they me effete: hence the albuminoid principles have been termed the *tic* materials of nutrition, in order to distinguish them from rs portions of the food which, like starch and fatty matters, are cially needed for maintaining the function of respiration, and h have been termed the *respiratory* materials of the food. It however, be necessary to consider the components of food more etail (1506), after the properties of the albuminoid principles been discussed.

The albuminoid principles may be preserved in a dry state for ndefinite period without change, but if exposed to the air while t, they *gradually putrify* and emit a sickening odour. According to Lehmann, among the products of putrefaction are always to be found carbonate, butyrate, valerate, and hydrosulphate of ammonia, together with leucine and tyrosine. The readiness with which the albuminoid bodies putrify and undergo spontaneous chemical changes when moist is one of their most striking characters. Synaptase, diastase, pepsin, and other ferments are considered by Liebig to be modifications of albumen in particular states of decay; and yeast itself, although an organized structure, is supposed to owe a part of its remarkable power of exciting fermentation, to the presence of azotised matter which is undergoing definite transformation, although the nature of the change is but little understood. If albuminoid matters be heated in close vessels, they first swell up and fuse, then blacken, and emit a large quantity of fœtid empyreumatic products, among which ammonia and sulphuretted hydrogen are always present; and they leave in the retort a porous, brilliant, carbonaceous mass. When incinerated they furnish a notable amount of ash: this varies in quantity in different cases, but it always contains phosphate of lime.

(1447) All of these albuminoid substances are capable of existing both in a soluble and an insoluble form. In the animal fluids they occur in the soluble modification, whilst in the solid parts they frequently are found in the insoluble condition. The power of thus existing either in the solid or in the liquid state is of the greatest importance to the operations of animal life. It is necessary that these essential constituents of our frame should be able to exist in solution, in order that by the circulation of the blood they may be carried into every part of the body; and it is also necessary that they should be able to assume a solid form, to prevent the circulating fluids in their course from dissolving and washing away the delicate organs through which they pass.

These albuminoid principles, either in their soluble or their insoluble condition, are readily dissolved by the aid of a gentle heat in a solution of potash or of soda: the addition of an acid to the liquid so obtained causes the separation of a greyish flocculent precipitate, termed by Mulder *protein*, while a slight odour of sulphuretted hydrogen is emitted, vnd a small quantity of phosphoric acid is also found in the solution. This precipitation is best effected by means of acetic acid, since the mineral acids are obstinately retained by the flocculi. When either of these principles, in its soluble form, is evaporated at a gentle heat, it yields a semi-transparent friable mass, nearly insoluble in alcohol and in ether.

l, the addition of alcohol to the aqueous solutions causes their lation. Their aqueous solutions are also precipitated by the on of solutions of the salts of copper, of lead, and of mer- as well as by infusion of galls.

oncentrated sulphuric acid dissolves the albuminoid substances a brownish red colour, but the most characteristic tests for the minoid bodies are afforded by nitric and hydrochloric acids. entrated nitric acid produces in their solutions a coagulum of ght orange colour, and gradually dissolves it with efferves- ; or if they be in the insoluble condition, the tissue is stained w, and is slowly dissolved. Mulder considers this yellow ance to be a distinct compound, and names it *xanthroproteic* Concentrated hydrochloric acid when gently warmed with minoid solutions produces a milk-white coagulum, which it ves slowly, forming a blue or violet-coloured liquid. It may r be stated that acids generally produce coagulation of albu- d substances when in solution, but that (with the exception metaphosphoric) when added in excess they redissolve the lum. On diluting these acid liquids with a moderate quan- f water, a precipitate occurs, but it disappears if the dilution rried still farther. These acid solutions give a precipitate the ferrocyanide and with the ferricyanide of potassium, h the aqueous solution does not. Millon proposed to test e protein-compounds by moistening the tissues supposed to in them with a solution of two parts of mercury in four of acid, of sp. gr. 1·40. On the application of a temperature e below that of boiling water, an intense red colour is de- ed, which is not destroyed by boiling with water, nor by ure to the air. The gelatigenous tissues, however, produce lar coloration. This red colour is so intense that it may be ved on adding the mercurial solution to a liquid containing ore than $\frac{1}{100000}$th of its weight of albumen.

oth albumen and fibrin contain a small quantity (less than 2 nt.) of sulphur and of phosphorus; casein likewise contains ur, but phosphorus is absent. It is owing to the presence phur that putrid eggs possess their peculiarly offensive odour. ulphur is in the unoxidized condition, and this probably is he case with the phosphorus. By the action of a solution of , both these elements are in great measure removed from the c body, and when the alkaline liquid is neutralized with an he so called protein is precipitated, whilst the phosphorus and of the sulphur remain in the solution. The presence of un- ed *sulphur in the supernatant* liquid may be shown by adding to the cold solution in potash, of one of these compounds (albumen for example), a few drops of a clear solution of oxide of lead in potash, formed by adding an excess of potash to a solution of acetate of lead. On applying heat to the solution, the albumen is decomposed, its sulphur is removed, whilst sulphide of potassium and hyposulphite of potash are produced; $S_4 + 3(KO,HO) = K_2S_2 + H_2O_2 + KO,S_2HO_3$: the sulphide immediately shows itself by forming a brown precipitate of sulphide of lead, which renders the liquid dark-coloured and opaque: $PbO + KS = PbS + KO$. The phosphorus becomes oxidized and converted into phosphoric acid; it remains in the liquid, in which it may be discovered by the appropriate tests.

Many chemists, including Gerhardt among the number, regard all the substances of the albuminoid group as chemically identical, and as resulting from the combination of a single principle, which presents the characters of a feeble acid; the modifications in properties which it exhibits under the various forms of albumen, fibrin, and casein, being due to its combination with different bases, or saline bodies. This hypothesis, however, though probable, has not been actually proved to be true, and in the present state of science it is necessary to regard these bodies as distinct substances, which are convertible by vital processes one into the other, but each of which has its own peculiar functions in the organism.

The original view of Mulder was, that albumen, fibrin, and casein were derivatives of one fundamental azotised principle, which he termed *protein*; and that this substance by its union with different proportions of sulphur and of phosphorus, gave rise to the different modifications of the albuminoid group. Liebig has, however, shown that Mulder's protein always retains a small but variable amount of sulphur, and he denies the existence of protein as a separate body. It appears most likely that the substance termed protein by Mulder is merely the original body which was operated upon, but slightly modified in the course of the experiments by the action of potash. The following table indicates the composition of 100 parts of protein according to the analysis of Mulder, and it gives a comparative view of the results of the analysis of albumen, fibrin, and casein, by the same chemist, from which it is apparent that the composition of these bodies is such that mere ultimate analyses are insufficient to distinguish between them. The analyses of legumin are discordant, and it is very doubtful whether Dumas and Cahours operated on a homogeneous substance (1454). In all cases the ashes have been deducted previous to calculating the composition in 100 parts:—

	Mulder.					Gobley.	Dumas and Cahours.	Bence Jones.
nts.	Protein from Albumen.	Albumen from hen's eggs.	Fibrin.	Casein.	Globulin.	Vitellin from hen's eggs.	Legumin from peas.	Legumin from beans.
.	53·7	53·5	52·7	53·83	54·5	52·26	50·53	55·05
gen	7·0	7·0	6·9	7.15	6·9	7·25	6·91	7·59
en .	14·2	15·5	15·4	15·65	16·5	15·06	18·15	15·89
n .	23·5	22·0	23·5	22·52	22·1	23·24	24·41	
r .	1·6	1·6	1·2	0·85		1·17		21·47
horus		0·4	0·3			1·02		
	100·0	100·0	100·0	100·0	100·0	100·00	100·00	100·00

he numerous experiments upon fibrin, albumen, and casein,
subsequently to these, by various chemists, completely confirm
curacy of the results obtained by Mulder with these substances.

448) *Protein ?* ($C_{36}H_{27}N_4O_{12}=C_{36}H_{25}N_4O_{10},2\,HO$?).—Mul-
ill maintains the existence of a substance free from sulphur,
he terms protein, and to which he assigns the formula above
It has, however, never been procured free from sulphur.
elatinous flocculi, obtained on neutralizing an alkaline solu-
f any albuminoid substance, if well washed, and dried, furnish
wish, horny-looking, semi-transparent mass, which has, ac-
g to Mulder, the same composition, whether it be prepared
albumen, from fibrin, or from casein. Protein is destitute
te and smell: it is insoluble in water, alcohol, and ether;
water it swells up and becomes gelatinous in appearance.
kalies dissolve it, and deposit it unaltered on neutralizing
lution with an acid. In the mineral acids it swells up and
a jelly which retains a portion of acid; this acid jelly is
ble in water, though an excess of the acid dissolves it,
posits it unaltered on dilution. Diluted sulphuric acid if
d upon protein at 212° for some hours gradually decomposes
produces amongst other compounds a quantity of leucine.
hen protein, or any compound which furnishes it, is boiled
er for several consecutive hours, the protein gradually com-
with oxygen, and becomes converted into a soluble substance,
by Mulder *teroxide of protein and ammonia* ($H_4NO,2\,C_{36}$
$O_{13},3\,HO$?) : this compound is insoluble in alcohol and in
Its aqueous solution is precipitated by the mineral acids,
tions of chlorine, of tannic acid, and by the salts of lead,
r, of zinc, and of iron; but not by ferrocyanide of potas-
or by salts of baryta. It forms neutral compounds with
alies; *but if boiled with an* excess of potash or of soda it

with protein. This substan
yields the ammoniacal teroxi
ammoniacal teroxide appears
which is formed upon the sur
from patients suffering from c
In such cases, it is associated
nally described by Mulder as
chemist also regards this ins
constituent of the hair: it is
alkalies, and is sparingly so in
is this compound which const
from fibrin after it has been
is probably similar to that fo
substance, and its relations to
Indeed, the existence of the w
distinct principles, must be ad

(1449) Albumen.—The
tion are subject to conside
nature of the substances with
tions of albumen from the
therefore, differ in some resp
contained in the serum of blo
soluble albumen freed as far

solution being greatly promoted by the addition of a small ntity of chloride of sodium or of any other salt of the alkalies. nsiderable portion of the albumen is, however, always left in insoluble form. If white of egg, or serum, be evaporated to ness *in vacuo*, then powdered and digested in a small quantity cold water, the greater portion of the soluble salts is dis-ved, and at the same time a considerable quantity of albumen ound in the liquid; the residue, after being thus freed from its ble salts, is almost insoluble. Albumen, in its purest form, a slightly acid reaction upon litmus.

The most remarkable peculiarity of albumen is its power of difying on the application of heat and of becoming insoluble. s coagulation begins at 140°; the solution, if concentrated, sets a gelatinous mass, as is seen in the common process of boiling egg hard; but when the liquid is very dilute, it simply becomes bid. The albumen may, however, be separated by ebullition, vided that the solution be neutral or slightly acid; it then lects into flakes, which can be separated by filtration. Nothing known of the cause of the coagulation of albumen by heat. en a solution of albumen containing alkali, such as serum or ite of egg, is heated, a small quantity of sulphur is separated, the liquid becomes rather more alkaline from the liberation portion of the soda from the coagulated mass.

Coagulated albumen, when dried, forms hard, horny, trans-ent masses, of a yellowish colour. When plunged into cold er it absorbs four or five times its bulk of this liquid, and omes opaque and elastic. It is not soluble in water, but by boiling in open vessels it undergoes gradual decomposition, a soluble compound is obtained, which has the composition of xide of protein and ammonia (1448). If heated to 300° with all quantity of water, in a sealed tube, the albumen is redis-ed, and furnishes a liquid which does not coagulate by heat, which when acidulated with acetic acid gives a precipitate ferrocyanide of potassium.

Strong alcohol precipitates albumen from its aqueous solution; if the alcohol be rendered slightly alkaline by the addition of sh, no coagulation ensues. Ether, if free from alcohol, does not sion the coagulation of albumen, although it renders its con-d solution viscid. Kreasote occasions its immediate coagu- The concentrated mineral acids precipitate albumen in a l form, but gradually decompose it and dissolve it, it as they do upon the compounds of protein generally; solves *it with a* brownish-red colour, nitric acid produces with it a lemon-yellow, and warm hydrochloric acid a violet-coloured solution after some hours' digestion. Nitric acid precipitates it, and when dilute does not redissolve the precipitate. Hydrochloric acid precipitates it and redissolves the coagulum; the solution when poured into a small quantity of water becomes milky, but is rendered clear by the further addition of water. Dilute sulphuric acid produces no precipitate till the liquid is boiled; the clear solution in concentrated sulphuric acid is not precipitated when diluted with water. Metaphosphoric acid causes an immediate coagulation of albumen; but the other varieties of phosphoric acid produce no such effect. Acetic acid, and the organic acids generally, except the modification of tannic acid which is contained in infusion of galls, do not produce any precipitate in solutions of albumen.

The solutions of albumen in the organic acids are not coagulated by boiling, but a pellicle is gradually formed over the surface during evaporation; the addition of a saline solution, such as sulphate of soda or chloride of sodium, causes the albumen to separate from these solutions. The precipitates thus obtained are generally soluble in pure water; *precipitated* albumen is, therefore, not necessarily in the *coagulated* form. If a solution of white of egg be rendered accurately neutral by the addition of acetic acid, and then be diluted, flocculi of albumen are precipitated, but they are redissolved when treated with a solution of common salt or of nitre.

Solutions of alum, and of many of the metallic salts, such as those of copper, of lead, of mercury, and of silver, precipitate solutions of albumen. It is, therefore, useful to administer whites of eggs in the liquid form in cases where poisoning from swallowing any of the salts of these metals is suspected to have occurred; the remedy is a safe one, whilst if the poison have really been taken, the albumen decomposes the salt, and generally enters into combination both with the acid and the base; the albumen sheathing the stomach from the influence of the poison, whilst other measures are in preparation for effecting its removal from the system.

Effect of Bases on Albumen.—The presence of an alkali in liquids containing albumen considerably modifies the reactions; if the alkali be present in large quantity, the solution does not coagulate when heated, but a pellicle is formed over the surface during the evaporation, an appearance being thus produced similar to that observed when milk and other solutions of casein are exposed to the air whilst hot.

Albumen forms definite compounds with the alkalies and other llic oxides. Coagulated albumen is dissolved freely by solu- of the alkalies, and in certain proportions it even neutralizes action upon test-paper. If a concentrated solution of albu- be mixed with one of potash, a gelatinous mass of *albuminate tash* is formed, from which, by washing with cold water, the s of alkali may be removed; it retains 5·4 per cent of potash erkuhn). If the gelatinous mass be washed with alcohol and with water, it is insoluble in boiling water and also in boiling ol; but if it be washed with cold water only, the residue is le both in boiling water and in boiling alcohol. The aqueous ion of albuminate of potash is not coagulated by boiling it, on the addition of a small quantity of acetic, tartaric, or horic acid, a white coagulum is produced, which is readily lved by an excess of the acid. These characters resemble of casein, and some chemists have supposed that casein is ly an albuminate of potash. The coagulum obtained by the tion of acetic acid to the solution of albuminate of potash, well washed, furnishes nearly pure albumen. It leaves ely any ash on incineration.

The albuminate of *soda* resembles that of potash, and may be ed in a similar manner. The animal fluids in which albumen rs, such as the white of the egg and the serum of the blood, very slightly alkaline, the proportion of alkali not exceeding per cent. in ovalbumen (Lehmann). Even this small pro- on renders the albumen more soluble, and prevents its com- coagulation on boiling, a portion of albumen remaining lved and forming what is often termed *albuminate* of soda: and portion of the albumen which does coagulate does not collect flocculi. The albuminate of soda may be readily decomposed eutralizing it with acetic acid; on afterwards boiling it, the men is separated in coherent flocks. It is also to be remarked the albumen may be made to separate from the slightly ine liquid by boiling it after the addition of a neutral salt, as sulphate of soda, common salt, or muriate of ammonia. e are points which require attention in the analysis of animal ds, in which the quantitative separation of albumen is necessary. ardt is disposed to view serum and the white of eggs as contain- definite bialbuminate of soda; and adopting Lieberkuhn's for- for albumen, it would be ($HO,NaO,C_{144}H_{110}N_{18}S_2O_{42}+2\,Aq$). formulæ, however, can only be regarded as approximations.

According to Lieberkuhn, the compound of albumen with *of silver* is ($AgO,HO,C_{144}H_{110}N_{18}S_2O_{42}+2\,Aq$); that of copper $nO,C_{144}H_{110}N_{18}S_2O_{42}+2\,Aq$); the latter s[illegible]e is soluble in

mercury is formed when a solution of white of
one of corrosive sublimate: it is very insolu
but it is dissolved by a solution of common sal

Preparation.—The preparation of pure alb
lated form may be effected by precipitating whi
of hydrochloric acid, washing with the same aci
and then dissolving in water: this solution is
bonate of ammonia; the coagulum is washed
quently powdered, after which it is digested in a
in order to remove traces of adhering fatty mat
lated albumen may also be obtained by decon
of potash by means of acetic acid.

In the *soluble form* it is doubtful whether i
the albumen perfectly from salts. One met
object is nearly attained consists in neutraliz
egg with acetic acid; the liquid is then evapo
a platinum capsule at a temperature below 1
powdered residue is digested in very weak alco

Wurtz considers that a pure soluble album
in the following manner: white of egg is well
its volume of water, and strained through linen
the membranous flocculi: the filtered portion
a solution of subacetate of lead, in quantity i
down the whole of the albumen. The copio

No method is known by which the absolute purity of albumen can be ascertained. Its combining proportion is also uncertain, since it forms no definite compound upon the purity of which a decided opinion can be formed.

Sources of Albumen.—Albumen is a very abundant constituent of the animal body: it constitutes about 7 per cent. of the entire mass of the blood; it is an essential component both of lymph and of chyle; and it is abundant in all serous exudations, although it is found in these fluids in smaller proportion than in the serum of the blood. It is also contained in large proportion in many of the soft solids of the body, as for example, in the brain, the kidneys, the liver, and the pancreas, in all of which it exists in the uncoagulated form. The liquid of the pancreas appears to be the only secretion in which it occurs in health. It is never found in the excreta except under the influence of disease: thus it is occasionally poured out from the mucous membrane of the bowels in cases of intestinal catarrh, and has been repeatedly found in the alvine dejections in cases of dysentery, as well as in those of Asiatic cholera. It is likewise often met with in the urine in acute febrile affections, as well as in some chronic affections of the heart, liver, and kidneys, especially in the disease known as *morbus Brightii.* Its occurrence in the ovum is general, and is familiarly illustrated in the case of the eggs of birds.

The juice of many plants, such as that of carrots, turnips, and cabbages, when heated, becomes turbid, from the coagulation of a substance which analysis shows to have the same composition as albumen, and with which it coincides in all important particulars. Wheat flour likewise contains an azotised substance which is soluble in cold water, forming a solution which yields greyish flocculi of albumen on evaporation.

Paralbumen is the name given by Scherer to a substance obtained from the liquid of ovarian dropsy. Its solution is precipitated by alcohol, but the flocculi are redissolved by water at 100°, and it is only imperfectly coagulated by heat. Many other varieties of albumen which have been described probably arise from the modifying effects of salts upon albumen.

(1450) *Globulin,* or *Crystallin,* is a substance which closely resembles albumen. It occurs mixed with albumen in the cells of the crystalline lens in a very concentrated solution, forming, according to Simon, from 10 to 14 per cent. of the dry lens.*

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* Lehmann, in his experiments upon this substance, appears not to have separated the albumen, and hence the description which he gives of it differs from that of Simon, who removed this impurity.

It also enters largely into the composition of the red globules of the blood, and has hence received its name. Globulin cannot be obtained in the soluble form free from salts. It may be extracted from the crystalline lens by rubbing up the lens in a mortar to break up the cells, evaporating to dryness at 212°, washing with ether and dilute alcohol to remove the fat, and then dissolving the crystallin out with hot alcohol, of sp. gr. 0·915. A large portion of crystallin separates on cooling; after it has been dried it is insoluble in water, and it is precipitated from its alcoholic solution by diluting it with water.

Globulin is distinguished from the soluble protein-compounds by the circumstance that it is precipitated both from acid and alkaline solutions by exactly neutralizing them. It rapidly putrefies, and its solution when boiled emits ammonia. Its reactions with the mineral acids and with kreasote resemble those of albumen.

Vitellin is the name which has been given to the albuminoid constituent of the yolk of the egg; the yellow colour of the yolk is, however, due to an oil containing phosphoric acid, which is dissolved readily by ether, whilst the vitellin is coagulated. This reaction with ether, and the fact that its aqueous solution is not precipitated by salts of lead and of copper, are the principal characters by which vitellin is distinguished from albumen. By this ultimate analysis it is found to contain more hydrogen and oxygen than albumen (see Table, p. 751). The yolk of the egg contains 16 or 17 per cent. of this substance. According to the experiments of Valenciennes and Fremy, the composition of the azotised constituent of the yolk of the egg varies in different classes of animals. These chemists have termed that obtained from the eggs of cartilaginous fishes, such as the ray, *Icthin*, and that obtained from the eggs of the turtle, *Emydin*.

(1451) FIBRIN.—This substance, like albumen, occurs in two distinct states, the solid and the liquid, during the life of the plant or animal, but on removing it from the living organism it undergoes speedy, and so-called spontaneous, coagulation—a circumstance by which fibrin is at once distinguished from all other analogous substances. It is contained in the blood in the liquid state, in a proportion not generally exceeding 2·5 parts in 1000, though it is liable to considerable variation in quantity under the influence of disease, being greatly increased in febrile and acute inflammatory affections, especially in rheumatism and pneumonia, where it has been found as high as 11·8 parts in 1000. In anæmic diseases, in typhus, chlorosis, &c., it is frequently, but not uniformly, slightly diminished, though by long fasting it is somewhat increased in quantity. Lymph does not usually contain more than 0·4 or 0·5 parts per 1000. In the chyle of animals it has been found to vary from 0·7 to 7·0 per 1000.

Fibrin, in the form of muscular tissue, constitutes a large proportion of the soft parts of animals. It occurs in muscle arranged in bundles of fibres, and from this circumstance the name of fibrin derives its origin. Muscular fibrin, however, presents several points of difference from the fibrin obtained from the blood. According to Liebig, fibrin may also be obtained from the juice of plants, and it exists in the gluten of wheat.

Preparation.—Blood-fibrin may be obtained in a state of tolerable purity by whipping up freshly drawn blood with a bundle of twigs: in the act of coagulation the fibrin attaches itself in soft, white, opaque, elastic strings to the twigs, and may be afterwards washed clean by maceration and kneading in water till it is free from colour. When dry, fibrin forms a horny, yellowish, or grey solid.

The reactions of fibrin in the solid form are similar to those of coagulated albumen, except that fibrin decomposes deutoxide of hydrogen with effervescence, whilst albumen produces no such effect; but fibrin by long boiling in water is also rendered equally inert. When fibrin is heated to 300° with a small quantity of water, in a sealed tube, it is redissolved, and forms a solution which becomes coagulated by acids, and resembles that formed by albumen under similar circumstances. The coagulation of fibrin is prevented by allowing the blood, at the moment of its efflux from the body, to mix with solutions of certain salts, such as carbonate or nitrate of potash, acetate or sulphate of soda, and chloride of sodium. The fibrin of venous blood, before exposure to the oxygen of the air, is freely soluble in a solution containing about one-sixth of its weight of nitre, as well as in similar solutions of the alkaline sulphates, acetates, phosphates, and chlorides. This solution becomes coagulated like albumen when heated, but is precipitated by acetic acid; when exposed to the air, the solution absorbs oxygen and deposits insoluble flocculi. Fibrin is freely soluble in dilute solutions of potash or of soda, and the alkaline liquid presents many of the characters of albuminate of soda, but on neutralizing the solution with acetic or phosphoric acid, the fibrin is re-precipitated: if the alkaline solution be mixed with metallic salts, it yields precipitates similar to those formed with albumen. The solutions, both of fibrin and of albumen, in acetic acid, are precipitated on the addition of ferrocyanide of potassium, a character by which they are at once distinguished from gelatin, which gives no precipitate under similar circumstances. If the acetic solution of fibrin be neutralized by potash, it is precipitated by the same reagents as albumen, but it does not become coagulated when heated. There is a marked difference between the action of oxygen upon albumen and fibrin. Scherer found that when freshly drawn serum, or white of egg, was exposed to the action of oxygen gas, confined over mercury, scarcely any absorption of the gas occurs, and little or no carbonic acid is evolved; coagulated fibrin, on the other hand, when exposed in a moist state to the air, gradually absorbs oxygen, and emits carbonic acid, and in a few days becomes putrid. By long boiling in water it is gradually dissolved, and becomes oxidized. Albumen is similarly altered. Analysis appeared to prove that fibrin is a body which is more highly oxidized than albumen (see Table, p. 751); and coagulated fibrin, as it exists in muscle, is also more fully oxidized than that which separates from the blood on standing. Lehmann's view, that blood-fibrin is a stage of transition between albuminous matter and the animal tissues, is thus rendered highly probable. It appears also, from the analyses of Dumas and others, to contain about 1 per cent. more of nitrogen than albumen.

(1452) *Varieties of Fibrin.*—The observations of Liebig on the different forms of fibrin are interesting. He finds that moist *blood-fibrin*, if left under water in a warm place in a vessel loosely covered, putrefies, and gradually becomes dissolved; in one of his experiments, after the fibrin had been macerating for a fortnight, a liquid was obtained which coagulated when heated, and presented many of the characters of a solution of albumen. The solution likewise contained leucine, and acetic and valeric acid, besides some other acid substances, which have been but incompletely examined. Hydrosulphate of ammonia was also formed. If the water in which the fibrin is digested be previously mixed with one-tenth of its bulk of hydrochloric acid, blood-fibrin swells up slowly into a gelatinous mass, which, on the addition of a stronger acid, shrinks to nearly its original volume, and again swells up when put into water, but it does not form a true solution.

The *fibrin of muscle*, on the contrary, after it has been well washed and pressed, to free it from soluble matters, is dissolved more or less completely by dilute hydrochloric acid. If the acid contained in this solution be neutralized by an alkali, a coagulum occurs which is readily dissolved by an excess of alkali, or even by lime-water; this latter solution becomes coagulated, on boiling, like white of egg. On the addition of ammonia to the solution of fibrin in hydrochloric acid, the muscle fibrin is precipitated, and may be purified by successive washings in water, alcohol, and ether. The muscle of different animals varies in solubility in dilute acid; that of the fowl, and of beef, was found to be almost wholly soluble, that of mutton was less so, whilst in the muscular fibrin of veal the insoluble portion amounted to nearly one-half; this residue contained the fat and the vascular portions, besides a quantity of fibrin which resembled blood-fibrin in characters. The soluble portion was found to contain less nitrogen than the blood-fibrin. When fibrin is treated with acetic acid, and viewed by the microscope, it is found to consist of two portions, one of which is granular, and soluble in acetic acid, while the other is fibrous and insoluble. The proportion of these two components differs widely in different specimens. The ultimate composition of these two constituents appears to be very nearly the same.

The portion of the gluten of wheat flour which is insoluble in hot alcohol, and in ether, is regarded by Liebig and by Dumas as coagulated fibrin. It is soluble in very dilute hydrochloric acid, like the fibrin of muscle.

(1453) Casein is found abundantly in milk, of which it constitutes nearly 3 per cent. Its solutions do not become coagulated by boiling; they, however, present a reaction nearly as characteristic: the hot liquid gradually absorbs oxygen, and in consequence, a pellicle, which is insoluble in water, is gradually formed upon the surface.

Preparation.—Casein, in the *soluble* form, as present in milk, appears to owe its solubility to the presence of a certain proportion of free alkali. It cannot be obtained free from salts. If skimmed milk be evaporated to dryness at a gentle heat, and then digested with ether to remove the fat, on treating the residue with water, the lactose and a portion of the casein are redissolved, and, on the addition of alcohol, a considerable portion of the lactose is separated. The alcoholic liquid contains casein, still contaminated with lactose and with salts.

Casein may be obtained in the *coagulated* form nearly pure by the following process:—Skimmed milk is to be curdled with dilute sulphuric acid. The curd, after being well washed with water, is to be dissolved in carbonate of soda, and suffered to stand undisturbed for twenty-four hours or more, to allow the oil to rise to the surface; this is to be skimmed off, and the casein again precipitated by an acid, and well washed; after repeating this opertion a second time, the coagulum is to be digested in alcohol and in ether, and again dried; but it cannot be perfectly freed from the saline matters, which adhere to it with great tenacity.

Casein may also be obtained by coagulating skimmed milk by means of hydrochloric acid, and washing the curd first with water, then with water acidulated with 2 or 3 per cent. of hydrochloric acid, and finally with pure water; a glutinous mass is thus obtained, which is slowly dissolved by digestion at 110° in a large quantity of water. The solution, after being filtered, is precipitated by the cautious addition of carbonate of ammonia, the coagulum is washed with water, and then digested successively with alcohol and ether.

Properties.—Casein in solution is immediately coagulated by acids. An excess of acetic or of oxalic acid dissolves the coagulum, but it is re-precipitated from its acetic solution on the addition of one of the mineral acids. According to Bouchardat, water, containing 1-2000th of its weight of hydrochloric acid, forms with casein a colourless solution, which produces left-handed rotation of a ray of polarized light. If these acid solutions be evaporated at a high temperature, a pellicle of insoluble casein is formed over their surface. Mulder considers that when the mineral acids are employed to coagulate casein, they form definite compounds with it; the acid may, however, be entirely removed by washing. With strong nitric, sulphuric, and hydrochloric acids, casein produces the same reactions as albumen; and its acetic solution gives a similar precipitate with ferrocyanide of potassium. Soluble casein is sparingly soluble in cold alcohol, but more freely so in hot alcohol. The stronger acids produce no precipitate in this alcoholic solution, which, however, is immediately coagulated by infusion of galls. The solubility of casein in water is not destroyed by the action of alcohol, for the residue obtained on evaporating both the aqueous and the alcoholic solutions to dryness may be redissolved in water.

Action of Bases and of Salts.—Coagulated casein is readily dissolved by solutions of the alkalies, and of the alkaline carbonates; and if the solution be very feebly alkaline, the alkaline reaction may be completely neutralized by the casein. Solutions of common salt, of nitrate of potash, and of muriate of ammonia, likewise dissolve casein with facility, and these solutions, when evaporated by the aid of heat, become covered with an insoluble pellicle. Casein also unites with the alkaline earths and forms compounds which are insoluble in water. If a piece of poor cheese, which consists principally of casein, be reduced to a paste with water, and mixed with slaked lime, it produces a tenacious lute, which sets very hard, and may be used for cementing pieces of broken earthenware. In consequence of the tendency to the formation of these insoluble compounds, a solution of casein is precipitated by salts of lime or by sulphate of magnesia, upon the application of heat to the mixture: this reaction is very characteristic of casein. Most of the metallic salts, such, for instance, as acetate and subacetate of lead, sulphate of copper, subnitrate of mercury, and corrosive sublimate, occasion precipitates in the cold with solutions of casein.

But the most important and remarkable form under which the coagulation of casein occurs, is that which is produced by the secretion from the mucous membrane of the stomach. Advantage is taken of this in the manufacture of cheese, which consists essentially of the coagulated casein of milk. The coagulation is effected by means of the substance called *rennet*, which consists of the inner membrane of the fourth stomach of the calf, after it has been salted and dried. When milk is maintained for a few hours at a gentle heat in contact with rennet (or with an infusion of rennet prepared at a low temperature), the casein becomes entirely coagulated, carrying with it the fatty matters which were held in suspension by the milk, and leaving a clear straw-coloured liquid known as *whey*. It was at one time supposed that the rennet acted by converting the sugar of milk into lactic acid, and that the lactic acid was the real agent in effecting the coagulation, but this view is no longer tenable, for it appears that the coagulation occurs equally well with milk which has been purposely rendered slightly alkaline (Selmi, Heintz), and with an aqueous solution of casein; the action of rennet is therefore as yet unexplained. The coagulum, or *curd* thus obtained, when submitted to strong pressure, forms cheese. This curd is dissolved with difficulty by alkaline solutions. New cheese has but little flavour; when kept for some time the fatty and nitrogenous substances undergo partial decomposition, and furnish ammonia, with valeric and butyric acids, and other compounds which impart pungency to old cheese.

Casein has not been detected with certainty anywhere but in the milk of animals, which contains it in very variable quantity, the amount depending greatly upon the period of lactation at which the milk is examined. Its amount also varies greatly in the milk of different species of animals. In the human female it has been found to constitute from 31 to 35 parts in 1000; in that of the cow, from 30 to 41; in that of the dog, from 80 to 146, and in that of the ass, from 19 to 23 parts in 1000.

(1454) *Legumin.*—The seeds of most leguminous plants, as well as the sweet and the bitter almond, contain a substance which presents a close analogy in properties with the casein of milk. Liebig indeed considers it to be identical with this substance, but the analyses of Dumas and Cahours indicate a difference in composition between the two bodies. There is however some doubt whether the chemists last named operated upon a homogeneous substance.

Legumin is usually extracted from peas or from almonds, by digesting the pulp of the crushed seeds in warm water for two or three hours. The undissolved portion is strained off by means of linen, and the turbid liquid is allowed to deposit the starch which it holds in suspension: it is then filtered and mixed with dilute acetic acid. A white flocculent precipitate is thus formed, which must be collected on a filter and washed. It is then dried, powdered, and digested, first in alcohol and afterwards in ether. In this form it was analysed by Dumas and Cahours. Rochleder however considers that it is not perfectly pure, since this substance is not entirely soluble in a cold concentrated solution of potash, which leaves a flocculent matter. The alkaline solution may be decanted from the undissolved flocculi, and again precipitated by the addition of acetic acid. The legumin thus obtained is regarded by Rochleder as pure, and yielded on analysis the same results as were furnished by casein.

According to Dumas and Cahours, legumin is precipitated from its concentrated solutions in pearly flocculi by the addition of acetic acid. It is redissolved by acetic acid in excess, and by many other vegetable acids; it is also soluble in ammonia and in dilute solutions of the alkalies. It is insoluble in boiling water, and in cold alcohol and ether. Cold water dissolves it in considerable quantity, and the liquid, when heated to ebullition, deposits it in flocculi resembling those of coagulated albumen. The aqueous solution of legumin obtained by digesting peas in water is not coagulated by heat, according to Liebig, but on evaporation it forms insoluble pellicles resembling those yielded by solutions of casein. Legumin is associated in the seed with considerable quantities of the phosphates of potash, of lime, and of magnesia. It is coagulated by rennet like the casein of milk, and the Chinese make a kind of cheese from peas and beans. Dried peas contain about one-fourth of their weight of legumin.

§ II. GELATIGENOUS SUBSTANCES.

(1455) The substances contained in the second group of azotised bodies have hitherto been found only in animals. They contain a smaller amount of carbon and a larger quantity of nitrogen than those of the albuminoid group. The proportion of sulphur is also considerably less. The gelatigenous bodies consist of two principal varieties; viz., those which yield *gelatin*, and those which yield *chondrin*; neither gelatin nor chondrin appears to exist in the soluble form in the animal body, but it is in all cases the result of the prolonged action of boiling water upon the gelatigenous or chondrin-producing tissues.

According to the researches of Mulder, of Scherer, of Fremy, and of other chemists, the composition of gelatin is identical with that of the tissue which yields it by boiling. Chevreul found that a given quantity of tendinous matter when converted into gelatin by boiling it with water was not altered in weight. The following table exhibits the composition of gelatin, chondrin, and some gelatigenous tissues:—

Components.	Fremy.	Scherer.	Mulder.		Scherer.
	Ossein.	Sclerotica.	Gelatin.	Chondrin.	Cartilage.
Carbon . . .	50·4	50·1	50·40	49·97	50·5
Hydrogen . .	6·5	7·1	6·64	6·63	7·0
Nitrogen . .	16·9	18·7	18·34	14·44	14·9
Sulphur . .	26·2	24·1	24·62	0·38	27·6
Oxygen . .				28·58	
	100·0	100·0	100·00	100·00	100·0

The quantity of nitrogen given in Fremy's analysis of ossein is probably too low, for the same chemist found in it upon another occasion as much as 17·86 per cent. of nitrogen. Schlieper has shown that gelatin and the gelatigenous tissues contain a small quantity of sulphur, amounting in isinglass to 0·6 per cent. It will be observed that the composition of chondrin differs from that of gelatin in containing more oxygen and less nitrogen; whilst the percentage of carbon and of hydrogen is the same in both substances.

(1456) Gelatin is an azotised principle which hitherto has been obtained from animal substances only. Certain structures (the principal of which are the white fibrous tissue, the cellular tissue, the skin, the serous membranes, and the organic constituent of bone), when boiled with water, yield a compound, which if the solution contain more than 1 per cent. of it, causes the liquid to gelatinize on cooling, hence its name of *gelatin*; this substance does not appear to exist in a free state, but is developed by the action of boiling water upon the tissues above mentioned: its solution, when evaporated to dryness, leaves a brownish-yellow transparent mass. *Isinglass* which is prepared from the inner membrane of the floating bladder of sturgeons and other fishes, when boiled with water, furnishes gelatin in a state of considerable purity. *Glue* is a variety of gelatin of inferior quality. *Size*, as prepared from parchment, is another form of gelatin which is met with in commerce.

Gelatin softens and swells up in cold water, but is not dissolved until the liquid is warmed; it is insoluble in alcohol and in ether. It may be precipitated from its aqueous solution by the addition of an excess of alcohol, when it falls in white flocculi, which are nearly free from saline compounds. Its solution is without taste or smell: it is abundantly precipitated by solutions of corrosive sublimate, and of bichloride of platinum, as well as by the infusion of galls. The compound which gelatin forms with tannic acid is the basis of leather; it is of a buff colour, and is formed even in very dilute solutions. Albumen is also precipitated by the same solutions, but gelatin may be distinguished from albumen, since it is not rendered turbid as albumen is by the addition of ferrocyanide of potassium to its solution in acetic acid. Salts of alumina, of lead, of copper, and of iron, do not produce any precipitates in a solution of gelatin; but if a solution of potash be added to the mixture of gelatin with alum, or with persulphate of iron, the subsulphate of alumina or of iron which is formed carries down a large proportion of gelatin. In a dissolved condition gelatin soon becomes acid on exposure to air, and then loses its gelatinous character. Gelatin is capable of dissolving a considerable quantity of phosphate of lime. By the frequent boiling of its aqueous solution, gelatin is converted into an isomeric compound which does not possess the faculty of gelatinizing as the liquid cools. Chlorine precipitates gelatin completely, forming with it a peculiar white elastic compound which appears to consist of gelatin in combination with hypochlorous acid; this compound when treated with ammonia, yields nitrogen, muriate of ammonia, and unchanged gelatin. Solutions of gelatin are not rendered turbid by the addition of acids. Concentrated sulphuric acid dissolves gelatin without change of colour, and gradually converts it into glycocine, leucine, and some other bodies. Gerhardt found that when isinglass was boiled for some days with dilute sulphuric acid, sulphate of ammonia was formed, and a considerable quantity of a saccharine body which was

: of the alcoholic fermentation. Nitric acid produces l from it amongst other substances.

ition of gelatin to which the alkalies have been added in ntity loses its faculty of gelatinizing, but the liquid on itralized gives no protein. Gelatin is decomposed by caline solutions; at a boiling temperature ammonia is id leucine and glycocine are amongst the products.

DRIN differs from gelatin in composition: it is also co- by the vegetable acids, such as acetic acid, as well as by by the neutral and the basic acetates of lead, none of d precipitates with gelatin. Most of these precipitates e in an excess of the precipitant.

lrin is obtained by boiling the cornea of the eye, or any rmanent cartilages, with water for some hours; it may tained from the primary cartilages prior to ossification. n gelatinizes on cooling. It is remarkable that when a cartilage becomes ossified, it yields not chondrin but boiling with water.

Preparation of Glue and Size.

The preparation of gelatin on a large scale gives rise to f industry of considerable importance, viz., the manufac- ie and size.

trongest glue is obtained from the parings of ox-hides, the ears and refuse trimmings of thick hides in general, d from 45 to 50 per cent. of glue. These clippings are d for some days in lime water, to remove the hair, the other impurities; they are then washed in cold water, aced to drain upon a sloping pavement, in layers of two ches thick, and are turned over once or twice a day; me thus absorbs carbonic acid from the air, and becomes into chalk; so that the injurious effects of lime at a at upon the gelatin are prevented. The washed clippings itroduced into a copper which is filled to two-thirds of its ith rain water, and furnished with a perforated false bot- ently the animal matters are put first of all into a coarse , and the whole is placed in the cauldron, a precaution ents the portions of skin, when they begin to gelatinize, ring to the bottom and sides of the boiler, and so be- rned; fresh portions of clippings are added as the animal adually sink down into the liquid which is kept gently A still better method consists in boiling the liquid by steam under moderate pressure, by which means the direct application of fire to the boiler is avoided. As soon as a portion of the liquid sets into a firm jelly on cooling, the fire is checked, and the solution is allowed to run into a deep vessel or *settling back*, where it is kept warm for some hours to allow the impurities to subside. The undissolved matters contained in the cloth are again boiled with water, and yield an inferior description of glue; if boiled a third time they give a still weaker gelatinous product or size: the refuse, after this treatment, may still be advantageously applied as manure.

From the settling back, the solution is transferred to long wooden boxes or coolers, in which it gelatinizes; when sufficiently solid it is removed, cut into blocks, and each block is split by a wire frame into slices. The slices of moist glue are then laid upon nets placed in a wooden frame, and are so arranged in lofts as to allow free circulation of air. These cakes of glue are turned over two or three times daily, and the marks which are seen upon the glue exposed for sale, are those left by the threads of the nets. This operation of drying is the most delicate part of the manufacture, since at this stage much of the success of the operation depends upon the state of the weather. A sudden rise of temperature might liquefy the whole: the occurrence of a fog might render it mouldy, or a frost might split all the cakes into fragments. Spring and autumn are found to be the most favourable seasons for the manufacture of glue. After the drying has proceeded to a certain extent in the open air, the process may advantageously be shortened by the use of artificial heat from a stove.

When glue is properly made, it should be of a pale brown colour, hard, brittle, and should break with a smooth, glassy fracture. Cold water does not dissolve glue, but merely softens it, and causes it to swell up.

Size is a less tenacious kind of glue, and is chiefly made from parings of parchment, and of the thinner kinds of skins. It is almost entirely used in the gelatinous condition, so that the precarious process of drying is dispensed with. Much of the gelatin at present sold in fine shreds for use in confectionary is obtained from clippings of hides, which are boiled with water till they form a very liquid size, which is allowed to become clear by standing, and is then dried in very thin sheets, and afterwards cut up into shreds.

Preparation of Leather.

(1458) The hides of animals, like the soft parts in general, are prone to putrefaction and decomposition, if kept in a flexible and moist condition, and when allowed to dry, they become too rigid and brittle to allow of their employment for a number of purposes, to which they would otherwise be admirably adapted.

The operations of the tanner have in view the preservation of the hide from decay, and the preparation of a material possessed of the requisite suppleness, tenacity, and power of resisting the action of moisture.

The hides of different animals vary very much in thickness. The hippopotamus is furnished with a hide which is in some parts between one and two inches thick, whilst the leather produced from the skins of the lamb and of the kid does not equal ordinary pasteboard in thickness.

The thicker kinds of leather receive the general name of *hides*; and the strongest parts of these hides, which cover the back of the animal, constitute the *butts*. Ox-hides, the most valuable of which are those imported from the plains of South America, and from the Cape of Good Hope, yield the principal portion of this leather, which is largely consumed for the soles of boots and shoes, for harness, and for articles requiring much strength and durability. The upper-leathers of boots and shoes are chiefly made of calves' and seals' skins; whilst for book-binding, for aprons, and for ordinary dyed leathers, the leather furnished by sheep skins constitutes the material principally used.

The skin of most animals is highly elastic; it consists of two portions which are quite distinct in chemical composition; an outer thin superficial layer, the *epidermis*, which dips down and lines the tubes containing the roots of the hair, and which rises in blisters after a scald. This is composed of a pellicle which resembles horny matter in composition; it is stained yellow permanently by the action of concentrated nitric acid: beneath this is the cellular layer, termed the *rete mucosum*, in which the colouring matter resides, but which is now generally regarded as a less compact portion of the epidermis: and below this is the thick sensitive vascular integument or *dermis*, which constitutes the true skin. When the dermis is boiled with water for some hours, it becomes dissolved, leaving the vascular parts, which can be removed by straining through linen or flannel; the clear liquid is nearly colourless; it gelatinizes on cooling, and consists mainly of gelatin. It gives with tincture of galls the well-known insoluble precipitate by which such solutions are characterized.

Excepting in those cases where it is desired to preserve the hair, as in the different species of furs, the preliminary steps in the preparation of all skins are pretty much the same, whatever the use to which the leather is applied, but greater care is requisite in the thinner kinds. After the hair has been removed, the preservative process differs with the nature of the skin to be operated on. Four principal processes are in use for the preparation of leather. They consist of—

1. *Tanning.*—This is employed for the thicker kinds of leather; it is essentially a process for combining the astringent principle of vegetables with the hide.

2. *Sumaching.*—This operation is similar in its results to tanning, but is less laborious and tedious; it is performed upon the thinner leathers or *skins,* which are often subsequently dyed.

3. *Tawing.*—This process is followed in preparing white and black kid, principally for the glover: in this operation alum and common salt are worked with some oily matter into the skin.

4. *Shamoying.*—This process is used in the preparation of wash-leather. It consists essentially in combining some suitable fatty matter with the texture of the softer part of the hide.

Liming, Unhairing, and Raising the Skin.—In all cases the first thing to be done is to cleanse the skin thoroughly from blood, from the salt used in preserving it, and from other extraneous matters. This is effected, in the case of recent hides, simply by washing, or, in those which have been salted, by soaking them for some days in pits in which the water is occasionally changed. It is frequently found advisable, in order to expedite this cleansing, to place the hides in the fulling-mill, where they are beaten with heavy hammers shod with iron, by which the skin is speedily rendered supple. The ears and projecting useless pieces having been removed, and disposed of to the glue-maker, the hides are generally transferred to pits containing lime-water, with an excess of lime, which gradually dissolves the sheath of the hairs, and combines with the fat; here they remain for three weeks or a month, and are transferred gradually from pits containing a weak lime-water to those in which the proportion of lime is much more considerable. In some of the French tanneries a weak solution of caustic soda has been substituted for lime-water, with considerable advantage; the skin is more rapidly prepared for unhairing, and the excess of caustic soda is afterwards much more readily removed than the excess of lime. Sometimes, instead of plunging the hides into lime-water, they are placed in a warm room till a slight degree of putrefaction commences; during this incipient putrescence ammonia is disengaged, and the hair becomes loosened as readily as when lime is used.

In order to remove the loosened hair, the hides are placed upon a sloping, semi-cylindrical table, with a rounded end, termed *the beam*, and upon this, with a two-handled knife, the hide is scraped on the hair side to remove the epidermis and hair. By this operation the upper surface of the cuticle marked by the insertions of the hair is exposed; it is of a denser structure than the layers of cuticle below, and it forms what is called the *grain* of the skin; great care is taken not to injure this grain, as such injury impairs the quality of the leather, and much reduces its value. The hair having been removed, the hide is once more rinsed and scraped upon the beam, on the flesh side, to remove any irregularities, and adhering loose cellular tissue.

The cleansed hide is then immersed for twelve hours in a bath of weak sulphuric acid and water (1 part of acid and 1000 of water), which *raises* the skin, that is to say, makes it swell, opens its pores, removes adhering lime, and fits it for the actual operation of tanning. Care must be taken to avoid an excess of sulphuric acid, as it is liable to injure the texture of the hide. The removal of lime from the skin is a process of great importance, since, owing to the circumstance of the astringent matter being of an acid character, it would combine with the lime, instead of with the gelatin, and would form a harsh, insoluble compound within the pores of the skin, which would impair the suppleness of the leather.

(1459) 1. *Tanning.*—Up to this point the preparation of the skin is very similar for each kind of leather; when the process of tanning is to be performed, it is conducted in the manner now to be described.

The process of tanning is a very slow one. A weak infusion of bark, called *ooze*, is first prepared and pumped off into rectangular pits, six or eight feet deep, sunk in the earth, and lined with wooden planking; into these the hides are introduced, one by one, in an extended state. These pits of weak ooze are termed *handlers*, from the circumstance that the hides are for some weeks daily transferred from one pit to another, into oozes of gradually increasing strength: in about six weeks they are ready for the pits termed *layers*. In these pits the partially tanned hides are placed, each hide being separated from the one above and the one below it by a layer of coarsely ground oak bark; the pits are then filled up with water. Here the hides remain for about three months, and are then transferred to another pit, and similarly treated; but the hides which before were uppermost, and consequently in the weakest part of the infusion, now are undermost, and in the strongest part. Sometimes the hides require to be passed a third time through the layers. At the end of this time, the skin, if of the thickness of a good ox-hide, will be completely tanned, as may be known by cutting it across with a knife, when it will appear of a uniform brown colour: a white line in the centre shows that this part is imperfectly tanned. About 300lb. of oak bark are required to tan 100lb. of fresh skin. They yield about 150lb. of leather.

From the tanpits the hides are removed to the drying-loft, where they are, in dry weather, exposed to a free current of air, assisted, when the weather is cold or damp, by heat, furnished by steam-pipes. When the leather is sufficiently dry, it is beaten upon a kind of horse, or cylindrical beam, and is subsequently rolled with a brass roller, loaded with a weight of from 10 to 20 cwt.

Many attempts have been made to shorten this tedious process, for example, either by the employment of stronger oozes at first; or by the operation of sewing up the hide, filling it with the tanning infusion, and allowing the liquid to force its own way through the pores of the hide, aided by the influence of gravitation; or by passing the hides between rollers, as they come out of the spent ooze, and then allowing them to be transferred to stronger ooze: but it has been generally found that the leather so prepared is harsher and less durable than that obtained in the old way. This is found especially to be the case in thick hides: the surface gets tanned hard in the strong ooze; the inner portions are by this means protected from the tanning action, and their complete conversion into leather, which is so desirable, is prevented. Moreover, it is found that it is useful that a certain portion of the gummy and mucilaginous matter contained in the bark should be absorbed by the hide; it increases the suppleness of the leather, and therefore renders it more durable: by the process of quick tanning, the quantity of mucilaginous matter which the hide takes up is materially and injuriously reduced.

Currying.—The thinner skins, such as are used for the upper-leather of boots and shoes, as well as the thicker kinds employed in the manufacture of hose, in some parts of harness, &c., have to undergo the further process of currying, the object of which is, by impregnating them with oil, to render them less pervious to water, and make them more supple and pliable, as well as to give them that gloss and finish which, in many cases, is considered essential.

In currying, the leather (a calf-skin, for example) is thoroughly soaked in water, and shaved while wet with a peculiar two-handled knife, upon a smooth, heavy, flat beam, faced with lignum vitæ, and placed nearly vertically, the object of this operation being to equalize the thickness of the skin in its different parts. It is then thrown into water and worked while moist upon a flat stone table with the flesh-side downwards. It is thus uniformly thinned out and stretched. Here it is next *stuffed* or *dubbed*, that is to say, it is thoroughly impregnated with a mixture of coarse fish-oil and tallow, after which it is hung up in a loft to dry and allow the oil completely to penetrate the leather and take the place of the water.

When dry, the skin is rendered supple and 'grained' by rubbing it first on the flesh side, after folding the grain side inwards, with a grooved ball of box-wood; the operation is then repeated on the grain side. In this state, after another scraping on the flesh side, or *whitening*, it is ready to be stored away. Previous to sale, however, another process, technically termed *waxing*, is performed. This consists merely in rubbing in upon the flesh side, a mixture of lampblack and oil, with a hard brush. A coat of tallow and size is then rubbed over this with a sponge; it is polished with a ball of glass, and a final coat of thin size completes the operations of the currier. For ladies' shoes the skin is blackened on the grain side, which is easily effected by rubbing it over with a solution of sulphate of iron; the astringent matter of the leather immediately strikes a deep inky black with the copperas; a weak alkaline liquid is brushed over the whole, the skin is allowed to dry, it is then grained, and finished off with a coat of oil and tallow.

Stenhouse finds that when shreds of thin leather, such as the upper-leather of shoes, are digested, under a pressure of two atmospheres, in a Papin's digester, with lime and a considerable quantity of water, the leather is almost entirely decomposed, the tannic acid combines with the lime, forming an insoluble compound, and a glue of good quality is obtained on evaporating the solution, amounting on the average to 25 per cent. of the leather employed. Thick sole-leather does not yield glue or gelatin when similarly treated. Analysis did not indicate any considerable difference in the composition of these different leathers. Even thin leathers, if kept for several years, lose the power of furnishing gelatin when decomposed by the foregoing method of treatment.

(1460) 2. *Morocco Leather.*—The thin kinds of leather which are dyed and used for ornamental purposes, as for coach linings, chair-covers, book-binding, &c., are tanned differently, but much more expeditiously than hides. The finest kind of this leather is made from the skin of the Barbary goat, and hence the term *Morocco leather* as commonly applied to it. In the preparation of these skins the wool or hair is removed in the usual way, and the lime is then worked out by a process termed *abating*. In this operation the skins are put into a weak solution of an ammoniacal salt (dogs' dung being the material preferred); the lime forms a soluble compound with the acid of the salt, setting ammonia at liberty; this softens the skin, and at length renders it so porous that when a portion of air is included in a fold of the skin the air may be squeezed through it. The skin is next cleansed on the beam, and is sewed up in the form of a bag, the grain side outwards, and is ready for the *sumaching*, or tanning, which is accomplished in about twenty-four hours. A weak and warm infusion of sumach is prepared in a large tub; a portion of sumach leaves and of a stronger infusion is poured into the bag formed by sewing up the skin, and this, when distended with air, is tied up and thrown into the vat, where the floating bags are kept in constant motion for some hours; after which they are piled up on a sloping shelf on the side of the vat, where, by mutual pressure, a portion of the tanning solution is forced through the pores of the skin. The operation is repeated with a stronger infusion of sumach; after which the skins are cut open, washed, dried, and subsequently dyed. In the operation of dyeing, the flesh sides of two of the moistened skins are placed in contact, and are made to adhere by striking them out and scraping them on a flat table, and the dyestuff is then applied to each skin in succession, by which means it is limited to the grain side. A *light blue* colour may be given to the skin by the use of a mixture of ferrocyanide of potassium and nitrate of iron; a *green* by a combination of the barberry with indigo; a *maroon* by a mixture of archil and ammonia with indigo; a *scarlet* by the action of cochineal, alum, and carbonate of potash; and a rich *purple*, known as *royal purple*, by means of indigo faced with cochineal. Red morocco is usually dyed before it is tanned with sumach.

(1461) 3. *Tawing.*—The thin and delicate skins which are employed in the manufacture of 'kid gloves' are subjected to a different and more careful process than that above described: they are first washed to free them from blood, and from the salt employed to preserve them from putrefaction, and are then anointed on the flesh side with cream of lime, and left for a few days; after which they are washed, and the hair is plucked off. They are then soaked in lime-water for a fortnight or three weeks, at the expiration of which time they are carefully smoothed with a whetstone upon a beam. The lime is next removed by soaking the skins in a mixture of bran and water, which has been allowed to become sour; the lactic acid which it contains forms a soluble salt with the lime, and at the same time swells the skin and opens its pores, reducing it to the form of a thin, white, extensible membrane, technically termed a *pelt*. In this condition it is ready for the operation of tawing, or passing through the *white bath*. Tawing, in fact, consists in preparing the skin with a solution of chloride of aluminum, and subsequently working in a quantity of oily and farinaceous matter.

This white bath is composed of a mixture of alum and common salt, dissolved in water in the proportion of 12 gallons of water to every 100 skins, and from 12 to 18lb. of alum and 2½ to 3lb. of salt: after the skins have been introduced into the mixture the temperature is gradually raised nearly to boiling. When the skins have been soaked for some time in the bath, they are thoroughly kneaded together by placing them in a revolving drum, by which means the liquor is well incorporated with them. They are next washed, first with water, then with a mixture of bran and water, and are dried, after which they are worked with the *paste*. In preparing this paste, about 3 gallons of the alum liquor are mixed with 13 or 14lb. of wheat flour and the yolks of 50 eggs, and in this bath the skins are worked separately, and allowed to remain for 24 hours: at the end of that time they are kneaded together by the action of the revolving drum; they are again dried; they are next dipped in water for a few minutes, and staked or stretched, and are worked upon the board with a softening iron, by which means they are greatly extended in all directions; after which they are stretched upon frames to prevent them from shrinking during the drying. When dry they are tinted, if necessary, with a mixture of whitening and ochre, and are finally polished and ironed.

(1462) 4. *Shamoying.*—The operation of shamoying consists in working into the skin a quantity of oil, which supplies the place of the vegetable astringent, or of the chloride of aluminum, in the processes of tanning and tawing. In preparing the skin for shamoying, the operations of unhairing, and of raising, are the same as in ordinary tanning. A large proportion of shamoyed leather forms what is known as *wash-leather*. This is made from sheepskins, which are split for the purpose by means of a machine contrived with this view: the grain side of the skin is used in the preparation of hat linings, and for other purposes where but little tenacity is requisite, whilst the flesh side is converted into wash-leather. After the skins have been soaked in bran and water, they are spread out upon a table, and lightly sprinkled with oil; they are then folded into balls, each containing 4 skins, and are beaten for two or three hours in the fulling stocks, with heavy wooden hammers faced with copper; after this they are opened out, again sprinkled with oil, and a second time passed through the fulling stocks, until they cease to appear greasy. They are next hung up in a warm room, where the oil absorbs oxygen; and this oiling and ventilation is repeated two or three times: the skins are then scraped, and scoured with a weak alkaline ley which saponifies the excess of the oil. Afterwards they are washed with water, dried at a gentle heat, and then smoothed and rolled. The thicker leather, known as *buckskin,* is prepared in a similar manner, but the skin used is not split, the grain being removed by means of a knife, which raises a sort of nap upon the surface, but does not cut the leather.

CHAPTER XII.

CHEMICAL PROPERTIES OF SOME OF THE SOLIDS AND FLUIDS OF ANIMAL ORIGIN.

§ I. *Solid Constituents of Animals.*

(1463) THE solid constituents of the animal body differ very materially from those of vegetables. The bony framework of the animal system contains a large proportion of inorganic insoluble salts; and the different tissues, into the composition of most of which nitrogen enters, vary widely from each other in chemical properties. It must not, however be supposed that any organ of the body consists of any chemical compound in a state even approaching to purity. The complex structure of these organs, consisting as they do of vascular, nervous, and cellular components, independently of the peculiar and proper substance of the organ itself, forbids the possibility of any such simple character in its chemical constitution, although one or two proximate principles may give to it the distinctive features which it offers to the chemist. The bones, the ligaments, the muscles, and the nerves, thus exhibit unmistakeable differences in chemical properties, owing to the predominance in each of certain proximate animal principles.

It will be useful to consider briefly the chief chemical characteristics of some of the most extensively diffused of these tissues.

(1464) *The Bones* present the same general properties throughout the higher classes of vertebrate animals. When dried at 212° till they cease to lose weight, they are found to consist of about one-third of their weight of organic matter; the remaining two-thirds being composed principally of phosphate and carbonate of lime and phosphate of magnesia. These facts may be readily verified:—if a bone, freed from fat and periosteum, be suspended in a vessel containing hydrochloric acid diluted with 6 or 8 parts of water, an effervescence will be seen to occur over the whole surface of the bone, owing to the decomposition of the carbonate of lime; in the course of three or four days the salts will have been dissolved out, and the remainder, which still retains the shape of the bone, will be found, after soaking in distilled water repeatedly renewed, to consist of the animal matter, or ossein only. Its rigidity will have disappeared, and it will have become perfectly flexible; but if it be dried, it will assume a semi-transparent appearance, resembling that of horn. When boiled for a few hours in water, it will be gradually dissolved, with the exception of a little fat and a few vascular and fibrous shreds, and the solution will gelatinize on cooling, forming a weak glue or size. The solution thus obtained is indeed nearly pure gelatin, and, like this substance, is precipitated copiously by tannic acid and by infusion of galls.

The acid solution when neutralized by ammonia deposits the earthy phosphates, which may be separated by filtration; and on adding to the clear liquid a solution of oxalate of ammonia, the lime which was contained as carbonate in the bone is precipitated.

Bones may be boiled for many hours in water without undergoing any further change than the separation of a quantity of grease, which rises to the surface of the liquid; but if placed with water in a Papin's digester and exposed to a temperature of about 300°, the gelatin is dissolved, and the earthy matters are left, and subside in a disintegrated form.

When bones are distilled in closed vessels at a gradually increasing temperature, a large quantity of fœtid, volatile, and tarry matters pass over, accompanied by a large proportion of carbonate of ammonia, and some other volatile alkalies formed on the type of ammonia. The residue in the retort constitutes animal charcoal, and contains the phosphate of lime with a quantity of carbon diffused through it in a very finely divided state. The saline components of the bone may be obtained in an isolated form by calcining bones for some hours in an open fire, when a white ash is left. The composition of bones differs slightly at different ages, and even in different parts of the body of the same animal. The *Teeth* are similar in composition to the bones, but the portion which projects over the gums is encased with a compact hard crust, known as the *enamel*, and which contains but a very small proportion of animal matter :—

Composition of Bones, &c., in 100 *parts.*

Constituents.	Heintz.			Berzelius.	
	Ox. Femur.	Sheep.	Man. Forearm.	Human. Tooth.	Human. Enamel.
Animal matter	30·58	26·54	31·11	28·0	2·0
Phosphate of lime . . .	57·67	61·99	59·14	64·3	88·5
Fluoride of calcium . .	2·69	2·79	2·23		
Carbonate of lime . . .	6·99	6·92	6·32	5·3	8·0
Phosphate of magnesia .	2·07	1·58	1·20	1·0	1·5
Other salts				1·4	

The bones of fishes contain a smaller proportion of phosphate of lime than is found in those of the higher orders of vertebrata. The scales of fishes have a composition somewhat similar to that of bone, but they contain phosphate of lime in small quantity only.

The proportion of earthy matter in the bones in the human species is occasionally deficient in certain forms of disease. In one instance of what the Germans call *cranio-tabes* in children, Schlossberger found the earthy salts to fall in the spongy portion of the bone as low as 28·16 per cent. of the dry bone, and in several cases the proportion of earthy matter was as low as 50 per cent.; similar facts have been noticed by other observers. Numerous analyses of the bones of different parts of the human body, in various conditions of health and of disease, and at different periods of life, have been executed by Von Bibra, who has published a special work upon the subject (*Chemische Untersuchungen über die Knochen und Zahne*); and an elaborate paper by Fremy, upon the hard parts of animals, has recently appeared in the *Annales de Chimie*, III. xliii. 47: many other writers might also be quoted. For fuller information on this subject, and on the chemical composition of the various tissues of the animal body generally, the reader is referred to Lehmann's treatise on *Physiological Chemistry*, a translation of which has been executed for the Cavendish Society by Dr. G. E. Day.

The organic matter contained in the envelope of the *Crustacea* consists of a substance termed *chitin*, which, according to Fremy, contains no nitrogen; both Schmidt and Lehmann, however, find nitrogen in this substance (1466). The animal component of the s of the *Mollusca* contains nitrogen, and has been termed by ny *conchioline:* it is distinct from albumen, and resembles n in composition, but when boiled does not furnish gelatin. hard covering of the *Crustacea,* and the shells of the *Mollusca* of the eggs of birds, contain but a very small proportion of sphate of lime, the principal earthy component in these cases isting of carbonate of lime. The subjoined analyses show the tesimal composition of some of these substances :—

Constituents.	Prout.	Bucholz.	Chevreul.	
	Shell of hen's egg.	Oyster shells.	Shell of crab.	Scales of perch.
imal matter	2·0	0·5	28·6	57·4
isphate of lime	1·0	1·2	6·0	37·8
rbonate of lime	97·0	98·3	62·8	3·0
sphate of magnesia			1·0	0·9
her salts			1·6	0·9

(1465) *Horny Matter.*—The composition of buck-horn and of y much resembles that of bone; but horny matter in general, ther in the shape of cow-horn, tortoise-shell, whale-bone, the s of beasts of prey, or the nails of the fingers and toes, the s of fishes, the feathers of birds, or the wool and hair of ani- generally, is of a different composition; it contains but little e matter, not exceeding 2 or 3 per cent., and does not furnish in when boiled with water at high temperatures under pres- It becomes soft on the application of heat, a circumstance h is turned to account in the manufacture of common articles rn, so that they can thus be moulded in some measure to the ed form. Horn is gradually and with difficulty dissolved by ne solutions, to which it yields up a portion of sulphur; and eutralizing the solution with an acid, a precipitate is formed h resembles that obtained from the albuminoid compounds: precipitate, however, presents properties which are slightly ent according to the nature of the source from which it is ed. If horny tissue be fused with hydrate of potash it is posed, evolving between 4 and 5 per cent. of amylia. Horny r is intermediate in composition between the albuminoid and genous components of the body. It contains less carbon and itrogen and sulphur than the albuminoid compounds. The g Table gives the composition of some of the different of these bodies.

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rer's analyses (*Liebig's Annal.* xl. 1) are calculated with *quivalent of carbon, 6·115.*

Constituents.	Scherer.				Fremy.	
	Epidermis (foot).	Hair (human).	Wool.	Quills.	Turtle shell.	Whale-bone.
Carbon . . .	51·04	50·62	50·65	52·42	53·6	50·8
Hydrogen . .	6·80	6·61	7·03	7·21	7·3	7·4
Nitrogen . . .	17·22	17·93	17·71	17·90	16·4	16·5
Sulphur . . .	24·94	24·84	24·61	22·47	2·0	25·3
Oxygen, &c. .					20·7	

Constituents.	Mulder.				Crookewit.	Schmidt.
	Nails (human).	Horn (cow).	Hoof (horse).	Sericin (silk).	Sponge.	Chitin.
Carbon . . .	50·3	50·0	50·4	48·61	46·51	46·64
Hydrogen . .	6·9	6·8	7·0	6·50	6·31	6·60
Nitrogen . . .	17·3	16·3	16·7	17·34	16·15	6·56
Sulphur . . .	3·2	3·4	3·0	27·55	0·50	40·20
Oxygen, &c. .	22·3	23·5	22·9		30·53	

From the foregoing Table it will be seen that horny matter differs but little from gelatin in ultimate composition; though in its reactions it more closely resembles the albuminoid group. Horny tissue is stained yellow by nitric acid. The quantity of sulphur in the hair is very considerable, and has been found to average from 3 to 5 per cent., though in some specimens of red hair Von Bibra found it to amount even to 8 per cent. The cause of the variety of the colours of the hair appears to be due to the variations in colour of the animal oil with which it is impregnated. The tint of the hair may be altered readily by steeping it in a solution of chlorine, as well as by moistening it with various nostrums which act upon the sulphur contained in the hair (758). The inorganic constituents of the feathers of birds vary in quantity in the different species from 1 to 6 or 7 per cent. (Gorup Besanez.) Silica is always present, and in the largest quantity in the feathers of granivorous birds, in which it forms on the average four-tenths of the entire earthy material. Silica is also found in the ashes of hair when burnt. In human hair the ash amounts to from 0·92 to 1·57 per cent.: and of this the silica constitutes nearly one-seventh. The hair and wool of animals contains in general rather more ash than human hair.

Silk.—This substance appears to consist of three distinct azotised components which are arranged in layers, the outer one of which is soluble in water, and, according to Mulder, consists of gelatin; it amounts to about one-fifth of the weight of the silk; beneath this outer layer is one of albumen, which is soluble in

e alkaline leys and in acetic acid, as well as in a solution of
lkaline soap, and beneath this is the substance mentioned as
in in the foregoing Table. The colour of the silk is due to a
ll quantity of oily matter. Gossamer threads also contain
cin. Sericin is a white silky-looking substance which is left
er successive exhaustion of the silk by water, alcohol, ether, and
ling acetic acid. It is insoluble in cold dilute alkaline solu-
s, but soluble in concentrated sulphuric and hydrochloric acids,
d in an ammoniacal solution of oxide of nickel.

The organic constituent of the *common sponge*, according to
lder, consists of *fibroin*, but it contains 1·9 per cent. of phos-
rus, and 1·08 of iodine. It is closely analogous to sericin, but
nsoluble in ammoniuret of nickel.

(1466) *Chitin* ($C_{17}H_{14}NO_{11}$? Schmidt; $C_{12}H_{10}O_{10}$? Fremy).—
substance mentioned as *chitin* in the foregoing Table, consti-
s the true skeleton of insects and crustacea generally. It may
btained by boiling the outer wing-cases of the cockchafer in
r, alcohol, ether, acetic acid, and solution of potash, in succes-
. According to Fremy, chitin is also readily procured by treat-
the shell of the lobster or of the crab with dilute hydrochloric
, then washing with water, boiling for some hours with a dilute
tion of potash, then with alcohol, with water, and with ether.
e chitin is a white substance, which retains the form of the
ure from which it is obtained. It is soluble in concentrated
c and hydrochloric acids without colouring them, and these
tions, after neutralization with ammonia, yield a precipitate
infusion of galls. Oil of vitriol gradually dissolves it, and
ly lets fall a black precipitate, whilst acetic acid and acetate
mmonia remain in solution, and sugar is also found to be
ent. When distilled it also yields acetic acid and acetate of
onia; boiling concentrated solution of potash does not affect
This substance, if it be azotised, is certainly one of the
lest forms of the nitrogenised plastic materials. It presents
points of analogy with vegetable fibre, particularly in the
ction of acetic acid by its decomposition. The compound to
h Fremy assigns a composition isomeric with that of cellulin
tinct from chitin. Berthelot calls it *tunicin*, from its entering
the composition of the envelope of some of the tunicate
usks. It yields, when treated with acids, products similar to
e furnished by chitin.

(1467) *Cartilage.*—The articular extremities of the bones are
rusted with a white elastic opaque horny substance which con-
s but little *saline admixture* (from 3 to 6 per cent. of salts),

and which by long boiling is gradually dissolved, forming a liquid which on cooling furnishes a tremulous jelly. The transparent cornea, the rings of the trachea, the elastic parts of the ears, nose, and eyelids, and the flexible prolongations of the ribs are also composed of the same material; this substance, however, is not true gelatin, but the modification of it termed *chondrin* (1456).

White fibrous tissue, and the material of which the tendons, ligaments, and inelastic tendinous expansions are composed, consist of a substance which by continued boiling is almost completely dissolved, and a solution of gelatin is formed, which gelatinizes on cooling. *Yellow fibrous tissue* has a different composition: it is insoluble in boiling water, and in weak acids and alkalies, but is readily soluble in hot concentrated sulphuric acid, and in a strong solution of potash. It resists putrefaction for a long time, and possesses great elasticity. Nitric acid forms a yellow compound with it. The yellow fibrous tissue is an advantageous source of leucine when digested with sulphuric acid which has been diluted with 1½ parts of water.

(1468) *Muscular tissue* consists principally of fibrin in a coagulated form, but being highly vascular, and containing nearly three-fourths of its weight of water, it is permeated with a fluid consisting partly of blood and partly of substances secreted from it, independently of a small proportion of nervous and adipose matter. If lean beef be minced fine, and digested in three-fourths of its weight of cold water and then expressed, this treatment being repeated twice, a solution will be obtained which contains in a concentrated form the soluble constituents of the muscular tissue. These consist chiefly of albumen, the soluble salts of the blood, of the crystallizable animal principles termed kreatine and inosin, of phosphoric acid, and at least three organic acids, viz., the lactic, the inosic,* and the butyric; possibly also acetic and formic acids are present in small quantity; the colour of the solution is due to the red colouring matter of the blood. The salts consist chiefly of phosphate of potash, phosphate of magnesia, and a small quantity of chloride of sodium, and of phosphate of lime.

When this expressed liquid is heated nearly to the boiling point, the albumen becomes coagulated, carrying with it a large proportion of the colouring matter; this coagulum generally amounts to between 2 and 3 per cent. of the fresh muscle operated on.

(1469) *Inosic acid* ($HO,C_{10}H_6N_2O_{10}$? Liebig).—This compound presents the appearance of a syrupy liquid, which is not soluble in alcohol. It has an agreeable taste of the juice of meat, and becomes readily decomposed, mere boiling of the solution producing its partial decomposition.

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* This acid, according to Gregory, is found only in the flesh of the common fowl and of the turkey.

Inosic acid may be prepared from the mother-liquor obtained from the flesh of the common fowl after the separation of the kreatine (1417): alcohol is to be added to this liquid till it becomes milky, when it is set aside to crystallize, and the inosates of baryta and potash are slowly deposited; they are dissolved in water, and chloride of barium is added to the hot aqueous solution; on cooling, the inosate of baryta crystallizes; by a second crystallization this salt is obtained in a state of purity, and the acid may be obtained from it by the cautious addition of sulphuric acid.

The salts which inosic acid forms with the alkalies may be crystallized. When decomposed by heat, they emit an agreeable smell of roast meat. *Inosate of potash* crystallizes in long delicate four-sided prisms, which are sparingly soluble in alcohol. Inosate of *baryta* crystallizes in scales of a pearly lustre, which effloresce in a dry air; they are sparingly soluble in cold water, but freely so in boiling water, and are insoluble in alcohol. Inosate of *copper* forms a light blue insoluble powder which is not dissolved by acetic acid.

(1470) *Inosin, Inosite,* or *Muscle Sugar* ($C_{12}H_{12}O_{12} + 4$ Aq).—This interesting body was discovered by Scherer in the juice of flesh: but according to Lehmann it is only found in the involuntary muscles, the heart yielding it most readily; it has been found in the urine in Bright's disease (Cloetta), and in the same secretion in diabetes (Hohl). It may be obtained by the following process:—After separating the kreatine by crystallization, the baryta is removed by the cautious addition of sulphuric acid so long as it occasions a precipitate. The liquid is then filtered, and the free lactic acid separated by repeatedly washing with ether. Alcohol is added to separate the salts; and by gradually increasing the quantity of alcohol, small crystals, resembling those of gypsum, are formed; these crystals consist of inosin. They must be redissolved in water, and recrystallized. Inosin has recently been shown by Hohl to be identical with phaseo-mannite, which is obtained from the seed of the common kidney-bean, *Phaseolus vulgaris.*

Inosin forms colourless efflorescent prisms, which lose nearly 17 per cent., or 4 equivalents, of water at a temperature somewhat below 212°. The residue has then the composition of grape-sugar which has been dried at 212°. At 410° the dry mass melts to a colourless liquid, which, on cooling quickly, sets into a crystalline mass. It has a sweet taste, and is freely soluble in water, less so in rectified spirit, and is insoluble in absolute alcohol and in ether. Dilute acids and alkalies, even when boiled with it, produce no change. Its solution has no rotatory action upon a ray of polarized light. With concentrated nitric acid it yields a nitro-substitution compound. A solution of inosin to which caustic potash has been added dissolves hydrated oxide of copper with a blue colour, but does not reduce it to suboxide when the liquid is boiled. The solution of inosin gives a white precipitate when mixed with one of basic acetate of lead. Inosin is not susceptible of the vinous fermentation, but with chalk and cheese it yields lactic and butyric acids.

(1471) *Chemical Effects of Cooking upon Food.*—A consideration of the chemical constituents of muscular tissue enables us readily to understand the principal changes produced in the cooking of meat. The common processes of cooking have been very clearly explained by Liebig.

The operation of *roasting* consists in the gradual coagulation of the albumen, as the heat penetrates from the surface towards the interior: those parts which are nearest the centre, unless the roasting be continued for a sufficient length of time, do not become hot enough to allow the albumen to coagulate; hence they appear red, juicy, and *underdone* as it is called; the superficial portions become brown, and partially altered in composition, but the greater part of the sapid and saline constituents of the juices contained in the meat are retained, although a certain proportion exudes, and a part of the fat is melted off, and collects below, as *dripping*.

In *boiling* meat the result is somewhat different: when the flesh is placed in cold water, and the heat is gradually raised, the soluble albumen, the soluble salts, and the flavouring portions of the meat (which is contained entirely in the soluble parts) begin to pass out into the water, and the meat gradually becomes impoverished, while the liquid in which it is boiled gains in a corresponding degree in flavour and nutritive qualities—the meat becoming hard, ragged, fibrous, and tasteless at the surface, owing to the loss of its albuminous cement. When the water boils, the heat gradually penetrates the mass of the flesh, and as soon as it has risen high enough to coagulate the albumen which is still left in the central portions, the joint is said to be cooked through.

In order to preserve the full flavour of the meat during the boiling, it is necessary to make the water boil before introducing the joint to be cooked, and then to maintain it gently simmering until every part of the mass has attained a temperature of at least 170° or 180°. By this treatment, the albumen contained in the superficial layer of the meat is suddenly coagulated, and thus offers an obstacle to the free escape of the soluble portions from within; the meat therefore is proportionately richer, whilst the broth suffers to the same extent.

Liebig has introduced an improved method of preparing strong meat tea for invalids, founded upon the foregoing considerations. Lean beef or other meat is minced finely while raw, mixed with an equal weight of cold water, and slowly heated to boiling. After boiling for a minute to coagulate the albumen, the liquid is strained through a cloth, and the fibrous portion exposed to pressure; the broth thus obtained is seasoned with the usual condiments, and furnishes a nutritive soup of excellent flavour, which would gain nothing by longer boiling, but it has little colour.

A still more nutritious broth may be obtained in the following manner:—Take one-third of a pound of raw beef or chicken, mince it very finely, and mix it with 14 ounces of cold distilled water, to which four drops of hydrochloric acid and from 10 to 18 grains of salt have been added; digest for an hour, and strain out the meat upon a hair sieve; wash the residue upon the sieve with 5 ounces of distilled water. In this way about a pint of a cold extract of meat is obtained, which may be taken cold, or if warm, it must not be heated above 120°. The whole of the uncoagulated albumen, one of the most nutritive constituents of the meat, is thus extracted and administered to the invalid; whereas, if the broth be boiled, the albumen becomes coagulated, and is skimmed off and wasted.

The undissolved fibrin when washed once or twice becomes hard and insipid, and is difficult of digestion. The dark colour of soup contributes scarcely anything to its flavour, but custom leads us to associate the idea of strength and flavour with its appearance. The brown tint which long boiling gives, may, as is well known in the kitchen, be supplied by a little burnt sugar, and thus the eye as well as the palate may be satisfied.

The antiseptic power of common salt in preserving meat has been known from time immemorial, but no satisfactory explanation of its mode of action has been given. The process of salting detracts considerably from the nutritive value of the flesh so preserved. When raw meat is salted, the liquid portion speedily begins to ooze out, and to dissolve the salt, forming what is commonly termed *brine*, which is a saturated solution of salt in the juice of the flesh; the meat thus becomes proportionately impoverished of its albumen and of its sapid and saline components, and at the same time is deprived of its tendency to putrefy.

(1472) *Components of the Brain.*—The chemical knowledge of the components of the brain and nervous system is less satisfactory than that of many of the foregoing substances. It may be observed that these organs are especially remarkable in a chemical point of view. Fremy, a few years ago, published an investigation upon their composition, which has since been confirmed by Von Bibra in its essential points. The brain contains a large proportion of albumen in the uncoagulated form; but it seems to owe its peculiar properties to the presence of a solid fatty acid, termed *cerebric acid*, which contains phosphorus, and to a liquid, oily acid, called *oleophosphoric acid;* the latter compound also contains phosphorus. In addition to these bodies, cholesterin, and the ordinary fats, stearin and olein, are likewise present.

The human brain contains in 100 parts, about 7 parts of albumen, 5 of the above-mentioned fats, and 80 of water.

Cerebric Acid is a feeble acid, which is met with in the brain partly uncombined, partly united with soda. It is a white solid, which may be obtained in crystalline grains, soluble in hot absolute alcohol and boiling ether, but sparingly soluble in cold ether. It is not soluble in water, but swells up like starch in this liquid: it melts at a somewhat elevated temperature, and at a little above its point of fusion begins to be decomposed. It burns with a characteristic odour, leaving a charcoal which, owing to the formation of phosphoric acid, has an acid reaction.

Cerebric acid gave to analysis the following numbers, from which, however, no satisfactory formula can be deduced:—

Carbon	66·7
Hydrogen	10·6
Nitrogen	2·3
Phosphorus	0·9
Oxygen	19·5
	100·0

Oleophosphoric Acid is a greasy oil, which is insoluble in cold alcohol, but is readily dissolved by ether and by boiling alcohol. It appears to exist in the brain partially in the free state, but principally in combination with soda, with which it forms a soapy pound. This acid, according to Gobley, is likewise present in yolk of the egg. Oleophosphoric acid, by boiling it with r, is resolved into a mixture of olein and phosphoric acid, which r remains in solution. The presence of a free acid facilitates decomposition.

II. COMPOSITION AND PROPERTIES OF SOME OF THE MOST IMPORTANT ANIMAL FLUIDS.

The fluids contained in the animal body may be considered in following order :—

A. *Plastic nutrient liquids,* under which are included the *blood,* its tributaries the *chyle* and the *lymph ;* in connexion with ich it will be convenient to notice *milk.*

B. Liquids more or less necessary to the process of digestion, luding the *saliva,* the *gastric juice,* the *pancreatic fluid,* the *etions of the mucous membranes,* and the *bile.*

C. Excrementitious matter, comprising the *urine,* the *cutaneous etions,* and the solid *excrements ;* with which may be noticed , the product of the suppurative process.

A. *Plastic Nutrient Liquids.*—1. *The Blood.*

(1473) The blood is the most important of the fluids contained he animal system, since it supplies the material from which the ious organs of the body are derived. The remarks which follow r to the blood of the human species unless otherwise speci-

Since the blood is a fluid which consists of a mixture of a ety of different ingredients, and since it is every moment under- g changes of the most varied and complicated description, its position cannot be expected to exhibit the same definite acter as that of a crystallized mineral ; and yet there is con- rable uniformity in the chemical constitution of blood during th. In the vertebrate animals the blood is a somewhat viscid of a red colour, which is more or less bright according to the of the system from which the liquid has been taken ; that the arteries, or *arterial* blood, being of a florid red, whilst drawn from the veins, or *venous* blood, is of a dull purple. d has a peculiar odour, which differs somewhat in animals of rent species. This odour is more strongly developed by the tion of oil of vitriol to the blood. When left to itself, the d presents the remarkable phenomenon of coagulation, in equence of which it appears first to become semisolid, and tually it separates *into two* portions, one of which constitutes the solid *cruor* or *crassamentum,* and the other the liquid or *serous* portion. This coagulation generally commences in from three to five minutes after the blood has been drawn, and the clot continues to contract for ten or twelve hours. Coagulation is retarded by exposure to a low temperature; it occurs most rapidly at about 100° or 110°. The coagulation is due to the presence of fibrin, which exists in the blood in a state of solution whilst it is circulating in the living organism, but solidifies shortly after its removal from it: the cause of this coagulation is unknown. During coagulation the fibrin carries with it all the colouring matter of the blood, so that the clot has a deep red hue, and the serum is left colourless or straw-coloured. The reason of this complete separation of the colouring matter is revealed by the microscope. Blood, when exposed to a high magnifying power, is found not to be a homogeneous fluid, but to contain a multitude of small flattened disks, of a deep red colour, tolerably uniform in size in the same animal, but varying in magnitude and shape in different species of animals. These *blood disks,* or *red corpuscles,* float in a transparent, nearly colourless fluid, termed the *liquor sanguinis.* In human blood these red corpuscles are circular and slightly biconcave: in most other mammalia the blood disks are also circular; in birds they are elongated and oval, with an elevated centre; and in amphibia they are oval and slightly convex. These observations explain the cause of the complete separation of the colouring matter when the blood coagulates; since the fibrin, in the act of solidification, entangles the red corpuscles in its meshes, and mechanically separates them, just as white of egg removes the solid impurities suspended in syrup when it is used to clarify that liquid. If the blood be whipped with a bundle of twigs during the process of coagulation, the fibrin attaches itself in the form of white elastic filaments to the twigs, while the red particles are separated from it by the agitation. The defibrinated blood is of a deep red colour, and does not coagulate. Blood is prevented from coagulating by allowing it to flow from the vein into alkaline solutions, or into a concentrated solution of many salts of the alkalies, such as nitrate of potash, and sulphate and acetate of soda. In some cases of sudden death, the blood is also found to have lost its property of spontaneous coagulation. In certain states of the system, owing partly to the slower coagulation of the fibrin, the upper surface of the clot is entirely free from colouring particles, the red corpuscles subside, and leave a stratum of variable thickness and of yellowish colour; to this coating the name of the *buffy coat* of the blood has been given; it is sometimes spoken of as the *inflammatory* crust, owing to its frequent occurrence during inflammatory diseases.

(1474) *Composition of the Blood.*—The following substances have been found as normal constituents of the blood:—Albumen, fibrin, colouring matter or hæmatin, globulin; oleic, stearic, lactic, phosphoric, sulphuric, and hydrochloric acids, in combination with soda, potash, ammonia, lime, and magnesia; minute portions of cholesterin, and a small quantity of phosphorized fat (containing phospho-glyceric acid), which has probably a composition similar to that of the fatty matter of the brain. The blood likewise contains in solution oxygen and nitrogen, derived from the atmosphere, and carbonic acid, which is produced by the reaction of the oxygen upon the constituents of the blood. These gases may be displaced by transmitting a current of hydrogen through the liquid. Lehmann, by passing a current of hydrogen through ox-blood till it ceased to expel carbonic acid, and then adding acetic acid without admitting air, and again transmitting hydrogen, has shown, by the expulsion of carbonic acid which then ensued, that recent blood must contain a free alkaline carbonate, in quantity equal to about 0·1628 per cent. of its weight.

The following Table, based upon the observations of Schmidt and the analyses of Lehmann, is given by the latter chemist as representing the average quantitative relation of the principal constituents of normal blood. It will be observed that the blood is here regarded as composed of two portions, one consisting solely of the red particles, and the other of the liquid in which these red corpuscles are suspended, termed the *liquor sanguinis*, which consists of the serum holding fibrin in solution:—

Sp. gr. of Blood Corpuscles, 1·0885.		*Sp. gr. of Liquor Sanguinis*, 1·028.	
1000 parts of blood corpuscles contain:—		1000 parts of liquor sanguinis contain:—	
Water	688·00	Water	902·90
Solid constituents	312·00	Solid constituents	97·10
(consisting of)		(consisting of)	
Hæmatin (with iron)	16·75	Fibrin	4·05
Globulin and cell membrane	282·22	Albumen	78·84
Fat	2·31	Fat	1·72
Extractive matters	2·60	Extractive matters	3·94
Mineral substances (without iron)	8·12	Mineral substances	8·55
Chlorine	1·686	Chlorine	3·644
Sulphuric acid	0·066	Sulphuric acid	0·115
Phosphoric acid	1·134	Phosphoric acid	0·191
Potassium	3·328	Potassium	0·323
Sodium	1·052	Sodium	3·341
Oxygen	0·667	Oxygen	0·403
Phosphate of lime	0·114	Phosphate of lime	0·311
Phosphate of *magnesia*	0·073	Phosphate of magnesia	0·222

The ash of ox-blood contains about 6·84 per cent. of oxide of iron (Lehmann).

The following Table gives the results of the average composition of human blood in man and in woman, according to the analyses of A. Becquerel and Rodier :—

		Male.		Female.	
Specific gravity of defibrinated blood			1·0600		1·0575
Of serum			1·0280		1·0274
Water			779·00		791·10
Fibrin			2·20		2·20
Fatty matters,	Serolin	1·60	0·02	1·62	0·02
	Phosphorized fat		0·49		0·46
	Cholesterin		0·09		0·09
	Saponified fat		1·00		1·05
Albumen			69·40		70·50
Blood corpuscles			141·10		127·20
Extractive matters			6·80		7·40
			1000·10		1000·02
Salts	Chloride of sodium		3·10		3·90
	Other soluble salts		2·50		2·90
	Earthy phosphates		0·33		0·35
Metallic iron			0·57		0·54
			6·50		7·69

The average specific gravity of healthy human blood is from 1·052 to 1·057, but it is liable to considerable variation, principally owing to differences in the proportion of the red corpuscles: it is usually more dilute in the female than in the male. The density of the serum is more uniform, and is generally between 1·027 and 1·029. The serum is a somewhat alkaline, straw-coloured, highly albuminous liquid, which becomes coagulated and forms a semi-transparent jelly when heated to about 170°. Its average composition has been already given, under the head of liquor sanguinis, in the table quoted from Lehmann; but since the liquor sanguinis consists of serum holding fibrin in solution, fibrin must be deducted from the list of the components of the serum.

(1475) *Hæmatin*, or *Hæmatosin* ($C_{44}H_{22}N_3O_6Fe$? Mulder).—This substance is the true colouring principle of the blood, and is, in many respects, a remarkable compound. It is the principal constituent of the body that contains iron. Hæmatin presents a considerable analogy with the albuminous principles, and may, like them, exist either in a coagulated or an uncoagulated form.

It occurs in the blood in the soluble form, and, according to the analysis of Mulder, it contains 6·6 per cent. of metallic iron. It appears to be probable that, like the sulphur and the phosphorus in albumen, this iron is not combined with oxygen. The peculiar colour of hæmatin is manifestly not dependent upon the iron which it contains, since nearly the whole of this substance may be removed without affecting the dark brown colour of the hæmatin; for example, if hæmatin be allowed to remain for some time in contact with concentrated sulphuric acid, and the liquid be then diluted, an evolution of hydrogen will take place, and protosulphate of iron will be formed in the liquid. The insoluble residue thus obtained contains carbon, hydrogen, nitrogen, and oxygen, in the same proportion as in hæmatin from which the iron has not been removed. If chlorine be passed through a solution of hæmatin in water, sesquichloride of iron is formed, and a white precipitate, termed *chlorhæmatin*, is produced, which Mulder represents as ($C_{44}H_{22}N_3O_{24}Cl_6$, or $C_{44}H_{22}N_3O_6 + 6\,ClO_3$), a compound analogous to that which is formed with protein, when albumen, suspended in water, is similarly treated. Hæmatin constitutes but a small proportion of the red particles of the blood (according to Berzelius, about 1-20th), the remaining portion consisting chiefly of globulin.

It is difficult to obtain hæmatin in a state of purity, and as yet it has only been insulated in its coagulated form. Blood which has been freed from fibrin by agitation with twigs before coagulation, is to be mixed with about 8 times its bulk of a saturated solution of sulphate of soda. After standing for a few hours, the colouring matter subsides; it must be collected on a filter, and washed with a solution of sulphate of soda. If the residue upon the filter be now boiled with alcohol acidulated with sulphuric acid, the colouring matter is dissolved. The liquid must be filtered while hot, and a portion of globulin, which has been dissolved, is to be thrown down by the addition of carbonate of ammonia. The red liquid thus obtained is again to be filtered, and evaporated to dryness; after which the solid residue must be digested successively with water, alcohol, and ether, and again be dissolved in alcohol containing ammonia, by which the remaining portions of globulin will be separated in the insoluble form; the solution is then to be filtered and evaporated to dryness; after which everything that is soluble is to be removed by digestion with water. The residue is considered to be pure hæmatin.

Coagulated hæmatin as thus obtained forms a dark mass, which assumes a slight lustre on pressure. It is destitute of odour and of taste, and is insoluble in water, alcohol, ether, and the fatty and essential oils. It is, however, readily dissolved by weak alcohol which has been acidulated with sulphuric or hydrochloric acid: this solution is of a deep-brown colour, but it becomes blood red on the addition of an alkali. Water precipitates the acidulated alcoholic solution. Strong acids decompose hæmatin, and extract the greater portion of its iron. Aqueous solutions of the alkalies, both caustic and carbonated, dissolve it freely; when these solutions are boiled, the colour, which is at first bright red, passes through dull red into green. Hæmatin is precipitated completely from its ammoniacal solution in alcohol, by salts of silver, of lead, and of copper. According to Denis, 1000 parts of blood contain 0·56 of metallic iron; so that reckoning the quantity of blood in a man of average stature at 30lb., it would amount to about 120 grains of iron in the blood of the entire human body.

(1476) *Hæmatoidin.*—A remarkable modification of the colouring matter of the blood, to which the name of *hæmatoidin* or *hæmato-crystallin* has been given, has been observed to occur sometimes in old extravasations, and in certain forms of disease. The colouring matter assumes the shape of irregular crystalline fragments, or of perfectly formed transparent red rhombic prisms, which are very sparingly soluble in water; yielding a solution which becomes coagulated at about 145°. Alcohol and nitric acid also produce a precipitate in the liquid. The aqueous solution of hæmatoidin is precipitated by solutions of corrosive sublimate, of subnitrate of mercury, and of sulphate of copper. Acetic acid dissolves the crystals of hæmatoidin readily; ammonia produces a liquid of the colour of peach-blossoms; potash does not dissolve them, but changes the colour of the crystals to a dirty yellow. Lehmann has pointed out a method by which these crystals may be readily obtained from the blood of various animals, particularly from that of the guinea-pig, the rat, and the mouse. After the serum has been well drained from the clot, the coagulum is to be placed in a cloth, and the greater part of the colouring matter washed out by means of a small quantity of water. The deep red liquid thus obtained is to be filtered, and a current of oxygen gas transmitted through it for about half-an-hour: after this, a current of carbonic acid gas is to be transmitted through the solution, for about 15 minutes. During the latter process the liquid gradually becomes filled with small crystals which, if allowed to subside, can be separated from the liquid portion. Lehmann found that the formation of these crystals was favoured by the action of solar light, but the exact changes which attend their production are not understood. The crystals obtained from the blood of different animals present differences of form and of solubility. They are generally prismatic, but those of the rat and the mouse are tetrahedral, and are very sparingly soluble, requiring 600 parts of water for their solution. The ultimate analysis of hæmatoidin furnishes results almost identical with those obtained from albumen. The purified crystals from the blood of a dog contained from 0·7 to 0·9 per cent. of ash, more than half of which consisted of peroxide of iron; phosphoric acid was also present in considerable proportion.

Globulin.—The *globulin* with which the hæmatin is combined has already been described (1450) as a compound bearing a strong analogy to albumen; it is contained in a state approaching to purity in the crystalline lens, and it constitutes the most abundant ingredient in the blood-globules.

The combination of globulin with hæmatin, or *hæmato-globulin*, which is present in the red corpuscles, is very readily acted upon by oxygen, and by many other gases, and is concerned intimately with the changes produced in the blood during the process of respiration. Oxygen gas is absorbed by the red corpuscles when suspended in the serum or when dissolved in water, the liquid assuming a brilliant red colour, whilst a disengagement of carbonic acid gas occurs. It is owing to this action of oxygen that the upper portion of the coagulum in venous blood, which is the part most exposed to the action of the air, is of a brighter red than the lower portions of the clot. Carbonic acid is likewise absorbed by the red particles; their colour then becomes changed to a dull purple, but the brilliancy of the red hue may be restored by further exposure to the action of oxygen: many saline solutions, such as those of nitrate of potash, also restore the red colour, and a similar effect may be obtained if syrup be added to the liquid. The solution of the colouring matter in water also experiences similar modifications in colour. Sulphuretted hydrogen causes the colour to pass into a dull green, and the red hue cannot be afterwards restored. Protoxide of nitrogen colours hæmato-globulin purple, and oxygen reproduces the scarlet colour in blood which has been thus acted upon. Sulphurous acid, and acid gases in general, darken its colour, which is again restored by oxygen. Admixture with saline solutions also restores the red hue to blood which has been darkened by sulphurous acid. From these facts it is obvious that hæmato-globulin is a compound extremely prone to change under the influence of many reagents.

(1477) 2. Chyle.—The term *chyle* is applied to the liquid derived from the nutritive portions of the food, which are absorbed from the inner surface of the intestines by a set of vessels, termed the *lacteals*, which pour their contents into one large absorbent trunk, called the *thoracic duct*, by which the chyle, as fast as it is supplied, is emptied into the general current of the circulation. The chyle differs in its qualities according to the nature of the food which has been taken, and according to the situation in which it is collected for examination. When removed from the body, it, in the course of a few minutes, undergoes a spontaneous coagulation, owing to the presence of fibrin. In this respect chyle differs from all the other animal fluids, except the blood and the lymph.

Chyle is an opalescent fluid, of a yellowish white, or pale reddish colour. It has a somewhat saline mawkish taste, and a very feebly alkaline reaction: it is generally more or less milky, from its holding in suspension minute granules, and globules of fatty matter; this milkiness is particularly observable when the food has contained much fat. Chyle, when boiled, generally deposits a few albuminous flocculi. Few satisfactory opportunities have occurred for examining the composition of human chyle. The proportion of fibrin contained in the chyle of the lower animals is subject to considerable fluctuations. In the chyle of a horse it was found by Simon to amount to 0·44 parts per cent.; in that of a cat Nasse found 0·13 parts of fibrin; and Rees found 0·37 parts of fibrin per cent. in that of the ass. When collected from the lacteals, before passing through the mesenteric glands, chyle frequently does not coagulate spontaneously, and the coagulation only occurs fully in that taken from the thoracic duct.

It has been observed that the quantity of fibrin is greater in animals from which the chyle has been collected while fasting. The quantity of fibrin in the chyle is also increased after passing through the mesenteric glands, as though a considerable portion of fibrin were added during its transmission through these organs. It appears not to be improbable that the albuminous matters are gradually converted into fibrin during their passage through the vessels, in the same way that albumen is formed whilst the aliments are passing from the stomach through the small intestines; since the quantity of fibrin increases, the nearer it approaches to the point where the chyle empties itself into the general mass of the circulating fluid. A few blood corpuscles are found floating in the chyle when it has reached the thoracic duct; and, when viewed by the

ranules are seen in suspension,
scles, resembling those
globules of fat are
ct, the composition of
is far more dilute ; the
of the horse varying from
it rises as high as 22 per

ication of albumen, which
quantity varying from 1 to 5 or
has contained a larger or smaller
The chyle, on exposure to the air,
d colour, and thus approximates in
r to the blood. This colour becomes
r the liquid has passed through the

—This is a colourless, or yellowish fluid,
aintly alkaline reaction. It is procured from
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he presence of fibrin in solution; in consequence
agulates in a few minutes after it has been with-
e body, and forms a scanty colourless coagulum. The
brin in lymph from the human body, obtained in
ry, has been found to be between 0·3 and 0·5 per
horse it varied from 0·04 to 0·33 per cent. The
bumen in human lymph is stated to vary from 0·4 to
but in the latter case it is not improbable that the
ixed with effused serum.

. Milk.—This important secretion is produced by the
nd of the female animal of the order *Mammalia*, after
o young: from the circumstance that the milk con-
ntire food of the young animal for many months,
high degree of physiological interest in relation
y of food, and to the processes of nutrition and of

a liquid of a well-known yellowish, or bluish white
hich is produced by the presence of a large quantity
r in suspension. It has a sweet taste, a slight but
ur, and in woman and the herbivora it has a feebly

alkaline reaction: in the carnivora it is slightly acid. When allowed to stand undisturbed for a few hours, the greater part of the fatty matter rises to the surface, and forms the layer which constitutes cream. When viewed by the microscope in a very thin layer, milk appears to be transparent: it contains a large number of highly refracting, transparent, oily globules floating in a transparent liquid; these globules are contained in a very thin investing membrane, which is not visible till the milk is treated with dilute acetic acid. Agitation of the milk with ether does not dissolve the fat, but if a small quantity of potash be added to milk, and it be then shaken up with ether, the fat is completely dissolved, the pellicle which envelopes the globules having been removed by the action of the potash.

The object of churning, in the preparation of butter from cream, is to break up mechanically the little sacculi which enclose the oily matter, and thus to facilitate the agglomeration of the fatty particles into masses, and to favour the separation of the liquid constituents which enter into the formation of the *buttermilk*. The more completely the albuminous and caseous matters are washed away, and the more compactly the butter is pressed, the longer may the butter be preserved without becoming rancid, since the caseous matter acts as a ferment, which speedily effects a partial decomposition of the fat. The addition of salt to the butter, by retarding the decomposition of the azotised matter, preserves the fats unaltered for a considerable period.

In addition to oily matter, milk contains two other characteristic ingredients, viz., milk-sugar and casein, both of which are held in solution. Albumen is absent from this solution in its usual condition, but it is abundant in the *colostrum*, or milk which is first produced after the birth of the young animal. The quantity of albumen in the colostrum of the cow is so considerable, that it coagulates when heated. The colostrum is denser than normal milk; it has a yellowish colour, and approaches serum in quality. It is worthy of observation that the sugar contained in milk is of a kind which does not undergo alcoholic fermentation, and consequently is not liable to produce an evolution of carbonic acid during digestion, so that distension of the tender stomach and intestines of the young animal from this cause is guarded against.

The salts contained in milk consist of the chlorides of sodium and potassium, of phosphates of the alkalies, and of a certain proportion of soda and potash, which are combined with the casein and confer solubility upon it; in addition to which, phosphates of lime and of magnesia are also found in considerable quantity.

se phosphates are essential to the development of the bones of young animal. A minute quantity of oxide of iron, amount- according to Haidlen, to 0·47 per cent. of the entire amount of is also found in milk. No sulphates, lactates, or salts of nonia, are present in fresh milk. The quantity of salts found ow's milk usually amounts to about 0·7 per cent. In woman's it is about 0·2 per cent. The composition of milk varies, not in the different species of animals, but also in the same animal fferent periods of lactation, the proportion of butter being cially liable to fluctuation, and being greatly under the influ- of diet: it also appears that the milk last yielded during the of milking is the richest. The following table comprises the lts of the analysis of 100 parts of milk in various species nimals, and will give an idea of the general nature of this d:—

Constituents of Milk.		Woman.	Cow.	Goat.	Ass.	Sheep.	Bitch.
ter		88·6	87·4	82·0	90·5	85·6	66·3
ter		2·6	4·0	4·5	1·4	4·5	14·8
ar and soluble salts . .		4·9	5·0	4·5	6·4	4·2	2·9
ein and insoluble salts .		3·9	3·6	9·0	1·7	5·7	16·0
gr. varies . . .	from	1·030	1·030	1·036	1·023	1·035	1·033
	to	1·034	1·035		1·035	1·041	1·036

The spontaneous acidification of milk when kept, and the sequent curdling of the milk, as well as the action of acids erally, in coagulating milk, and the effect of various neutral s of the earths upon this liquid, have already been mentioned S, 1453).

B. *Liquids concerned in Digestion.*

(1480) 1. THE SALIVA.—This secretion is poured out by the otid and other glands, the ducts of which empty themselves the cavity of the mouth. Its chief use appears to be to icate and moisten the food, and to facilitate the act of deglu- n. The saliva varies in composition considerably in different nals. In man it is an opalescent, somewhat viscid liquid, which s remarkably on agitation. The quantity of fixed solids h it contains in solution was found by Lehmann to lie between 8, and 0·841 per cent., but it has been observed as high as per cent. In the dog the solids amount to about 1·03, and e horse to 1 per cent. In addition to epithelial particles, to the mucus derived from the mouth itself, the saliva contains a peculiar organic principle, termed *ptyalin,* which resembles albuminate of soda, and which is very prone to putrefaction. Ptyalin constitutes about one-third of the soluble solids of the saliva. It is characterized by its power of converting starch, even in the granular form, into dextrin and into sugar.

The saliva in health has a feebly alkaline reaction; its alkalinity is increased during mastication, and diminishes after the process of digestion is completed. In inflammatory affections of the *primæ viæ* the saliva is, however, generally acid, and the same fact has been observed in various other forms of inflammatory disease. The inorganic constituents of the saliva consist of soda, and salts of potash and soda, with a considerable quantity of the salts of lime, which is deposited from the saliva of many animals (the horse, for example) in the form of crystallized carbonate, when the secretion is exposed to the air and allowed to absorb carbonic acid. It likewise occasionally contains lactates of the alkalies. Saliva also always contains a small quantity of phosphate of lime. This phosphate of lime mingled with a variable proportion of carbonate of lime and of salivary mucus, constitutes those calculous concretions which sometimes form upon the teeth, and are known as *tartar.* Minute quantities of sulphocyanide of potassium are also present in the saliva, as may be proved by the red colour which it yields on the addition of a dilute solution of the perchloride of iron. When sulphur has been taken medicinally, Wright found the quantity of the sulphocyanide to be considerably increased. The sulphates are almost entirely absent from the ash of saliva.

(1481) 2. THE GASTRIC JUICE.—This important secretion is the principal agent in effecting the digestion of the albuminoid portions of the food, but it exerts scarcely any action upon the starchy and fatty constituents. The gastric juice, as its name implies, is poured out from the lining membrane of the stomach. Its composition varies at different times, in consequence of which, when obtained from an empty stomach, its reaction upon litmus paper is either neutral or slightly alkaline; but after the ingestion of food into the stomach, it is always acid. In this, which may be considered its normal state, the gastric juice is a clear colourless liquid, which has a peculiar odour, and a slightly saline and acid taste. It does not become turbid when boiled, and it is remarkable for its antiseptic powers. It may be kept for many days at 100° F. without exhibiting any tendency to become putrid. The nature of the acid contained in the gastric juice has been disputed, some chemists maintaining with Prout that it is ydrochloric, others with Blondlot, that it consists of phosphoric in the form of superphosphate of lime, and others, that it is osed of lactic acid. In truth it appears generally to consist mixture of hydrochloric and lactic acids. The principal saline ers present are common salt, with small quantities of the ides of calcium and of magnesium, lactate of soda, and traces osphate of lime and of iron. The quantity of phosphate of is very small, and the sulphates and phosphates of the alkalies lmost entirely wanting. In addition to these bodies, how- the gastric juice contains a small quantity of a peculiar ic compound, which has been termed *pepsin*, to which, in nction with the free acid, the remarkable solvent and diges- owers of the gastric juice are owing.

epsin is an albuminoid body, soluble in water, but insoluble ohol. Its aqueous solutions are precipitated by corrosive nate, by salts of lead, and by solutions of tannic acid. boiled it loses its peculiar power of effecting digestion. An ial gastric juice, which acts as a solvent upon muscular boiled eggs, and albuminoid substances generally, may be ned by digesting the mucous membrane of the stomach with m but very dilute solution of hydrochloric acid. Such a ion, if maintained at a temperature of 100° F., will in the course x or eight hours dissolve pieces of hard-boiled egg and of ; but the solutions thus obtained do not coagulate on the cation of heat. They contain what Prout terms *incipient* *nen*, which does not acquire its ordinary properties until after s been subjected to the action of the pancreatic and biliary tions. In preparing this artificial digestive liquid the mucous brane of the stomach of the pig is generally employed as the e of the pepsin, the most active portion being the glandular extending chiefly along the greater curvature towards the l.

the appendix to Lehmann's work (vol. iii. p. 503), it is on the authority of Gruenewaldt, who had an opportunity king experiments upon a woman suffering from a gastric , that the quantity of the gastric juice secreted in twenty- ours amounted to the enormous quantity of 31 lb.; but the r portion of this liquid was, of course, re-absorbed by the s surface. In this case the gastric juice was carefully ed by Schmidt. The following are his results. It had a of 1·020. When heated, it emitted an odour of butyric opionic acids, and was found to contain in 1000 parts :—

Water	954·13
Pepsin	0·78
Sugar, albuminates, lactic and butyric acids, and ammonia	38·43
Chloride of potassium	0·70
Chloride of sodium	4·26
Potash	0·17
Phosphate of lime	1·03
Phosphate of magnesia	0·47
Phosphate of iron	0·01

No free hydrochloric acid was found in this analysis; when the stomach of this patient was irritated by introducing instead of masticated food, free hydrochloric acid was obt from the gastric juice, which was secreted unmixed with sali

Schmidt found the quantity of free hydrochloric acid in gastric juice of dogs, when unmixed with saliva, to amount to 0·245 to 0·423 per cent. Small quantities of chloride of am nium were also present in it.

(1482) 3. THE PANCREATIC FLUID.—The secretion from pancreas resembles the saliva in some respects. It has an line reaction, and putrefies rapidly. It possesses the pow saccharifying starch in an eminent degree, so that it appea assist in an important manner in the assimilation of the am ceous portion of the food, which is not rendered soluble by action of the gastric juice. Bernard considers that one o chief functions is to aid in the assimilation of fatty substa but the investigations since made in Germany by several ca and experienced observers have thrown some doubt upon accuracy of this view. It is, however, certain that the panc fluid furnishes a very perfect emulsion when agitated with oil it has been found that such an emulsion continues to exhibi same milky appearance if left at rest for fifteen or twenty h Under these circumstances the emulsion, which at first h alkaline reaction, generally becomes acid, and butyric and volatile acids are found in the liquid. The liquid from the creas generally becomes coagulated when heated; it is one few secretions which contains albumen in the soluble form proportion of albumen having been found by Tiedeman Gmelin, in some cases, to amount to 4 per cent. of the liquid. They also ascertained the presence of albumen i secretion in the horse, the sheep, and the dog.

(1483) 4. MUCUS.—Those cavities of the body which c nicate with the external surface are lined with a peculiar kind of membrane, distinguished as the mucous membrane. The material of which these membranes consist appears closely to resemble albumen in its coagulated state, but it is covered with a pavement of nucleated epithelium cells, which are continually undergoing gradual disintegration and solution. A tough viscid secretion, termed *mucus*, constantly bathes the surface of these membranes. In this secretion the epithelial particles can be traced in different stages of disintegration. The characters of mucus differ greatly with the surface from which it is obtained; but it usually assumes the appearance of a tough glairy semi-transparent mass, which swells up in water, but is not dissolved by this liquid. To the substance which gives it this glairy consistence, the name of *mucin* has been applied. Mucin is turned yellow by nitric acid; but it differs from albumen, since its solutions are not precipitated by corrosive sublimate; it is also not precipitated from its acid solutions by ferrocyanide of potassium until after the acid solution has been boiled. The mucus from the surface of the alimentary canal and its appendages is coagulated by acetic acid and weak acids in general, but it is soluble in alkaline solutions. The mucus from the surface of the urinary organs is dissolved to a certain extent both by acids and by alkalies. Both forms of mucus are immediately coagulated by alcohol, and the secretion presents many characters resembling those of a solution of albumen. Alkaline chlorides are abundant in mucus from the nose; and the phosphates of the alkalies and small quantities of the phosphates of the earths are also present.

(1484) 5. THE BILE.—This important secretion is produced from venous blood by the liver, and in most animals provision is made for its accumulation in a sac connected with the gland, termed the *gall bladder*. When taken from this receptacle it constitutes *gall*, or *cystic bile*.

Human bile is a ropy liquid, of a yellowish green colour when concentrated, but of a bright yellow when diluted. It has a peculiar musky odour and a bitter taste. When poured into water it sinks to the bottom, and does not readily mix with it, but it may be mixed with it by agitation, and it then forms a liquid which froths strongly, like a solution of soap. The viscidity of the bile is owing to the presence of a quantity of mucus from the gall bladder, which it holds in solution. Owing to the presence of this mucus the bile is very prone to putrefaction; but if the mucus be got rid of by coagulation with acetic acid and filtration, or otherwise, the bile may be preserved without decomposition for some time.

Ox bile, owing to the facility with which it may be procured, is the variety which has been chiefly examined. It has usually a sp. gr. of about 1·026, and, according to Berzelius, it contains the following ingredients in 100 parts:—

Water	90·44
Biliary and fatty bodies	8·00
Mucus	0·30
Watery extract, chlorides, phosphates, and lactates	0·85
Soda	0·41

No albumen is present in the bile, but its organic constituents contain a small percentage of nitrogen. It also contains sulphur in notable quantity. It is remarkable that the salts found in the bile of salt-water fishes consist almost exclusively of those of potash, while the salts of the bile of fresh-water fishes, and of the herbivora, consist chiefly of those of soda, although, from the circumstances in which the two classes of animals are placed, the opposite results might have been anticipated.

Owing to the facility with which bile undergoes decomposition, the statements of the earlier chemists who examined this liquid were contradictory; but the masterly researches of Strecker have at length removed all doubt respecting the true nature of the biliary secretion. The result of these investigations has been to show that ox bile may be regarded as a species of soap formed by the combination of two peculiar resinoid acids with soda. Both of these resinous acids (the *glycocholic* and the *taurocholic*) contain nitrogen. The taurocholic acid also contains sulphur, but the glycocholic acid is free from this element. Ox bile also contains, in addition to the mucus of the gall bladder, minute quantities of cholesterin, and a small amount of stearic, oleic, and lactic acids, united with potash and ammonia. Besides these substances a peculiar colouring matter is found in combination with an alkaline base, and a small proportion of a body called *lecithin* by Strecker, which is characterized by yielding oleophosphoric acid when boiled with hydrate of baryta.

(1485) *Glycocholic Acid;* (*Cholic Acid* of Strecker; $HO, C_{52}H_{42}NO_{11}$).—This acid constitutes the principal portion of the resinous matter of ox bile; it forms white, voluminous, silky, acicular crystals, which shrink much in drying; it is sparingly soluble in cold water, more freely so in hot water; the solution on cooling deposits crystals, which have a bitterish sweet taste.

ohol dissolves it freely, but leaves it as a resinous mass on poration: it is very sparingly soluble in ether. The salts which orms with the alkalies and the earths may be crystallized; they soluble in alcohol.

Glycocholic acid, when boiled with excess of an alkaline id, such as solution of baryta, undergoes a remarkable decomition: the whole of the nitrogen is separated in the form of cocine, which remains in the solution, and a new resinoid acid, *cholic* acid of Demarçay (*cholalic* acid of Strecker), is found in mbination with the baryta:—

$$\overbrace{HO,C_{52}H_{42}NO_{11}}^{\text{Glycocholic acid.}}+HO,BaO=\overbrace{BaO,C_{48}H_{39}O_9}^{\text{Cholate of baryta.}}+\overbrace{C_4H_5NO_4}^{\text{Glycocine.}}.$$

The elements of glycocholic acid, with those of two equivalents water, contain the elements of cholic acid and of glycocine; so t the decomposition of glycocholic acid by alkalies is analogous that of hippuric acid, by acids. If glycocholic acid be boiled h acids it gradually loses water, and becomes converted first o *cholonic acid* ($C_{52}H_{41}NO_{10}$), and then into glycocine and *loidic acid* ($C_{48}H_{39}O_9$; 1487), and the latter, by a further loss water, is ultimately converted into *dyslysin* ($C_{48}H_{36}O_6$).

Solutions of the neutral acetate of lead, of corrosive sublite, and of nitrate of silver, produce no precipitates in an aqueous ation of glycocholic acid. The salts which it forms with the alies are also unaffected by solution of chloride of barium; they are precipitated when mixed with solutions of the salts of per, of lead, of iron, and of silver. The silver precipitate is ewhat soluble in boiling water, and crystallizes as the solution ls. Acetic and other acids, when added to the solutions of the cocholates, decompose them, and throw down the acid in the n of a resin. *Glycocholate of soda* ($NaO,C_{52}H_{42}NO_{11}$) may obtained in crystals by the addition of three or four times its k of ether to its alcoholic solution, but it does not crystallize ter from water or from alcohol: it fuses easily to a resinous mass. e crystals have a very characteristic form; they consist of sixed prisms, with the ends obliquely truncated. The *crystallized* e of Platner consists of a mixture of the glycocholates of potash d soda.

Preparation.—Glycocholic acid is not obtained pure without siderable difficulty. Recent ox bile is evaporated, and the e is dried at a temperature of 250°; after which it is d with cold absolute alcohol. The solution thus obtained ed, and *ether is gradually* added, by which means a brown *mass is separated.* As soon as the liq [illegible] hus deposited most of the colouring matter, it is decanted, and the glycocholates of soda and potash, which are still retained in solution, are precipitated by the further addition of ether. The liquid becomes milky, a further separation of a resinoid substance occurs, after which the glycocholates are gradually deposited in the form of stellate tufts of needles. These crystals must be washed with anhydrous alcohol, containing one-tenth of its weight of ether, and then rapidly dried *in vacuo*. In order to obtain the acid, the crystals must be dissolved in water, and precipitated by dilute sulphuric acid; crystals of glycocholic acid are slowly deposited. This substance, however, is not pure even yet, for a part only of these crystals is soluble in water, scales of a body isomeric with glycocholic acid being left; this insoluble portion has been termed *paracholic acid* by Strecker. If paracholic acid be dissolved in alcohol, the addition of water precipitates it in the form of crystals of glycocholic acid.

(1486) *Cholic Acid* of Demarçay, *Cholalic Acid* of Strecker; ($HO,C_{48}H_{39}O_9+5$ Aq).—By adding hydrochloric acid drop by drop to the solution of cholate of baryta obtained by boiling glycocholic acid with baryta, the cholic acid is separated as a resinous mass; and this, on adding a small quantity of ether, is converted into colourless tetrahedra or octohedra, which are brittle and efflorescent. Cholic acid is very slightly soluble in water, forming with it a solution which distinctly reddens litmus. It is however freely soluble in alcohol, but less soluble in ether. The ethereal solution deposits the acid in rhombic tabular crystals which contain 2 Aq; this water of crystallization may be expelled by a gentle heat, after which the acid fuses at 383°, and a little beyond this it loses its basic water, and becomes converted into choloidic acid, and by a still further heat, into dyslysin (1487).

The cholates of the alkalies and of baryta are soluble in water and in alcohol; most of them may be crystallized from their alcoholic solution. The most characteristic test for cholic acid is furnished by treating it with sugar and sulphuric acid; an intense red colour, passing into a violet, is thus developed. Pettenkofer, to whom this observation is due, has founded upon it an excellent test for the presence of bile in organic fluids; cholic acid is formed by the action of the sulphuric acid upon the resinoid acids of the bile, and then furnishes the reaction in question. In order to apply this test, an alcoholic extract of the substance for examination is prepared, and dissolved in water; a drop of syrup consisting of 1 part of sugar to 4 of water is then added, and pure sulphuric acid free from sulphurous acid is cautiously poured in;

the liquid at first becomes turbid, but it clears as more acid is added, and passes in succession through cherry red, carmine, and purple into violet. The temperature must not be allowed to rise beyond 120° or 130°, and care must be taken not to use too much sugar, or it would be liable to become charred by the sulphuric acid. Acetic acid may be substituted for the syrup in applying this test.

Cholic acid approaches the fatty acids in character, and its salts are somewhat analogous to ordinary soaps.

(1487) *Choloidic Acid* ($C_{48}H_{39}O_9$).—Glycocholic acid is soluble in cold concentrated acetic, sulphuric, and hydrochloric acids without alteration, but it is decomposed when heated with them. If glycocholic acid be boiled with hydrochloric acid, glycocine is separated, and a new resinous acid, the *choloidic* of Demarçay, is produced; this acid contains an equivalent less of water than the cholic:—

$$2\,(\overbrace{HO,C_{52}H_{42}NO_{11}}^{\text{Glycocholic acid.}})+H_2O_2=2\,\overbrace{C_{48}H_{39}O_9}^{\text{Choloidic acid.}}+2\,\overbrace{C_4H_5NO_4}^{\text{Glycocine.}}.$$

Choloidic acid is a resinous, white, friable substance, freely soluble in alcohol, scarcely soluble in ether, and insoluble in water. It reddens litmus, and when treated with sulphuric acid and sugar produces the same reactions as cholic acid. The alkaline choloidates are soluble in alcohol and in water, but they do not crystallize: choloidate of baryta is insoluble in water. These salts are isomeric with the cholates, but do not at all resemble them. Choloidic acid is stated to contain no basic water, but this appears to be doubtful.

Both cholic and choloidic acids, like oleic acid, when distilled with nitric acid yield, by oxidation, the volatile fatty acids of the group $C_{2n}H_{2n}O_4$; acetic, butyric, caproic, œnanthylic, caprylic, pelargonic, and capric acids having been discovered in the results of the distillation by Redtenbacher. Various other oxidized products remain in the retort, among which are oxalic and cholesteric acids (1490), and a crystallizable body termed *choloidanic* acid ($C_{32}H_{24}O_{14}$).

By long boiling with hydrochloric acid, the choloidic acid in turn is decomposed; it loses 3 more equivalents of water, and becomes converted into a neutral resin ($C_{48}H_{36}O_6$), fusible at 284°, and which, from its difficult solubility in ordinary solvents, Berzelius called *dyslysin*.

(1488) *Taurocholic Acid; Choleic Acid* of Strecker ($HO, C_{52}H_{44}NO_{13}S_2$).—The sulphuretted acid of ox bile is the less abundant of its two components; though it is the principal ingredient in the bile of serpents, of fishes, and of some other animals; it does not appear to have been isolated in a perfectly pure state. It has however been ascertained that it gives rise, by treatment with acids, to cholic or to choloidic acid, and to dyslysin, but instead of glycocine it furnishes a remarkable crystallizable body, which contains all the sulphur of the acid; this substance has been named *taurin* ($C_4H_7NO_6S_2$):—

$$\overbrace{HO,C_{52}H_{44}NO_{13}S_2}^{\text{Taurocholic acid.}}+H_2O_2=\overbrace{C_4H_7NO_6S_2}^{\text{Taurin.}}+\overbrace{HO,C_{48}H_{39}O_9}^{\text{Cholic acid.}}.$$

Preparation.—In order to obtain taurocholic acid of tolerable purity, the following method recommended by Heintz may be employed:—To an aqueous solution of ox bile, neutral acetate of lead is added so long as it occasions a precipitate; the mucus, the oily acids, and the principal part of the glycocholic acid are thus thrown down, and must be separated by filtration. To the clear liquid a solution of subacetate of lead must next be added in small quantities at a time, until the successive precipitates become quite white, and assume a plaster-like consistence, when the liquid must be again filtered, and precipitated by the addition of an excess of basic acetate of lead mixed with free ammonia. This precipitate, which consists almost entirely of taurocholate of lead, must be purified by solution in alcohol, and reprecipitation by water; after which it must be decomposed by the action of sulphuretted hydrogen, and the taurocholic acid may be obtained by evaporating the solution, after filtering it to remove the sulphide of lead.

The taurocholates of the alkalies are very soluble in water and in alcohol. They give no precipitate with neutral salts of lead, but with basic salts of this metal slowly deposit a plaster-like compound, which is soluble in boiling water. They yield with sulphuric acid and sugar a violet colour similar to that produced by the cholates.

The bile of most animals yields taurin when treated with the concentrated mineral acids, since the occurrence of taurocholic acid is almost universal in this secretion, but the other resinoid acid varies in different classes of animals; that obtained from the bile of the pig, for example, is termed *hyocholic acid* and contains ($HO,C_{54}H_{42}NO_9$). Hyocholic acid yields glycocine when boiled with acids, whilst a new resinoid acid, the *hyocholalic* ($HO,C_{50}H_{39}O_7$), is separated. The compound which hyocholic acid forms with oxide of lead does not possess the fusible plaster-like character which distinguishes the lead salts of glycocholic and taurocholic acids. By long boiling with acids hyocholic acid is converted into glycocine, and *hyodyslysin* ($C_{50}H_{38}O_6$) which is homologous with dyslysin, but contains (C_2H_2) more than the latter compound. Hyocholic acid itself is homologous with *cholonic acid* ($HO,C_{52}H_{40}NO_9$), the resinous acid produced by boiling glycocholic acid with water, which under these circumstances loses two equivalents of water. *Hyocholeic acid* ($HO,C_{54}H_{44}NO_{11}S_2$), the sulphuretted acid of pigs' bile, bears a similar relation in its composition to taurocholic acid that the hyocholic does to glycocholic acid; that is to say, it contains 2 equivalents of oxygen less, and 2 equivalents of carbon more, than taurocholic acid. Quite recently Strecker has discovered in the pig's bile a small quantity of a new base, which he terms *choline* ($C_{16}H_{13}NO_2$).

(1489) *Taurin* ($C_4H_7NO_6S_2$).—This remarkable substance is readily prepared by freeing fresh bile from mucus by the addition of an acid, and filtering it; the clarified bile is then boiled for some hours with hydrochloric acid; the liquid decanted from the resinous acids is evaporated on the water-bath nearly to dryness, and decanted from the crystals of chloride of sodium which have separated: the mother liquor is then mixed with 5 or 6 times its bulk of alcohol, and the liquid on cooling yields crystals of taurin, which must be purified by recrystallization from water. The crystals of taurin assume the form of a six-sided prism terminated by four and six-sided pyramids resembling those of quartz. Taurin has a cooling taste; it is soluble in about 16 parts of cold water, but is not soluble in absolute alcohol or in ether. The mineral acids dissolve taurin without alteration, but do not combine with it, and even when heated with it they do not decompose it. Taurin contains more than 25 per cent. of sulphur, but is a compound of remarkable stability. When burned in the open air it emits abundance of sulphurous acid. A solution of caustic potash dissolves it, and if boiled down with it nearly to dryness, decomposes it, ammonia being evolved abundantly, whilst sulphurous and acetic acids remain in combination with the potash. Hence it appears that the sulphur is already in an oxidized condition. Taurin is isomeric with bisulphite of aldehyd-ammonia, a compound which may be prepared artificially, but which differs in properties from taurin; $C_4H_4O_2,H_3N,S_2O_4=C_4H_7NO_6S_2$. Strecker (*Chem. Gaz.*, 1854, 388) has however succeeded in procuring taurin artificially from isethionate of ammonia. Isethionic acid is prepared by absorbing olefiant gas by means of anhydrous sulphuric acid, and the product thus obtained is dissolved in water; on neutralizing the liquid with ammonia, and evaporating it until crystals are formed on cooling, the isethionate of ammonia ($H_4NO,C_4H_5S_2O_7$) is obtained. Now this salt contains the elements of taurin and 2 equivalents of water:—

$$\overbrace{H_4NO,C_4H_5S_2O_7}^{\text{Isethionate of ammonia.}} = H_2O_2 + \overbrace{C_4H_7NO_6S_2}^{\text{Taurin.}}.$$

On heating the isethionate gradually to 446°, it loses 11 per cent. of its weight, and the residue when dissolved in water yields by spontaneous evaporation crystals which have the form and properties of taurin from bile. Cloetta has found taurin in small quantity ready formed in the lungs of the ox; he has shown it to be the substance termed *pneumic* or *pulmonic* acid by Verdeil.

(1490) *Cholesterin* ($C_{52}H_{44}O_2 + 2\,Aq$?).—This crystallizable fatty body constitutes a never-failing ingredient of healthy bile, though, according to Berzelius, it does not exceed in quantity one part in 10,000 of the bile. It is probably held in solution by the agency of taurocholic acid, which possesses a certain solvent power over cholesterin. It acquires its chief interest and importance from the circumstance that, owing to its extreme insolubility, it cannot be reabsorbed when once deposited, and hence it frequently accumulates in the gall-bladder, and forms the principal ingredient in the most common variety of *gall-stone* or biliary calculus. Cholesterin is found also as a normal constituent of the blood; it is present in the brain in considerable quantity; it is also a constituent of the yolk of the egg, and in small proportion is a very frequent component of serous and fibrous exudations. It appears likewise to be always present in pus.

Preparation.—Gall-stones which contain cholesterin have a crystalline structure, and fuse on the application of heat, and they often have a specific gravity less than that of water. Such calculi furnish the best source of cholesterin. In order to obtain it from them the powdered gall-stones should be boiled in alcohol; the solution as it cools deposits characteristic rhombic plates of cholesterin, which, after one or two recrystallizations, is obtained in a pure state.

Cholesterin is nearly insoluble in water, but it is readily soluble in ether. When the ethereal solution is mixed with half its volume of alcohol and left to spontaneous evaporation, regular crystals are deposited; they contain about 5 per cent. of water: when heated to 212°, the crystals become opaque, and the water is expelled. Cholesterin fuses at 293°, and becomes crystalline on cooling; it may be distilled at a temperature of 660° without decomposition; but at a somewhat higher temperature it is partially decomposed. In the open air it burns with a smoky flame. The alkalies do not act upon it.

Berthelot finds that by heating together for some hours in a sealed tube with cholesterin various hydrated acids in excess, compounds may be obtained corresponding to the ethers of cholesterin, thus verifying the suggestion of Gerhardt, that cholesterin is a nobasic alcohol ($C_{52}H_{43}O,HO$). In this manner the following pounds have been formed :—

$$\overbrace{C_{52}H_{43}O,C_{8}\,H_{7}\,O_{3}}^{\text{Butyrocholesterin.}}=\overbrace{C_{52}H_{44}O_{2}}^{\text{Cholesterin.}}+\overbrace{C_{8}\,H_{8}\,O_{4}}^{\text{Butyric acid.}}-H_{2}O_{2};$$

$$\overbrace{C_{52}H_{43}O,C_{36}H_{35}O_{3}}^{\text{Stearocholesterin.}}=\overbrace{C_{52}H_{44}O_{2}}^{\text{Cholesterin.}}+\overbrace{C_{36}H_{36}O_{4}}^{\text{Stearic acid.}}-H_{2}O_{2};$$

$$\overbrace{C_{52}H_{43}O,C_{14}H_{5}\,O_{3}}^{\text{Benzocholesterin.}}=\overbrace{C_{52}H_{44}O_{2}}^{\text{Cholesterin,}}+\overbrace{C_{14}H_{6}\,O_{4}}^{\text{Benzoic acid.}}-H_{2}O_{2}.$$

se cholesteric ethers are white fusible compounds, sparingly ble in boiling alcohol, which may be employed to purify them unaltered cholesterin or acid. They are freely soluble in r, and are readily decomposed by heating them with an holic solution of potash.

Concentrated sulphuric acid decomposes cholesterin, by re- ing water and forming a mixture of three isomeric hydro- ons ($C_{52}H_{42}$) termed *cholesterilin*, which are distinguished by letters *a*, *b*, and *c*. These hydrocarbons bear the same rela- to cholesterin that olefiant gas does to ethylic alcohol. Long ing of cholesterin with nitric acid converts it first into a nous mass and then decomposes it, producing, amongst other ies, *cholesteric acid* ($HO,C_{8}H_{4}O_{4}$), which assumes the form of ght-yellow deliquescent substance, of an acid and bitter taste; s readily soluble in alcohol. According to Redtenbacher, the duction of acetic, butyric, caproic, and oxalic acids, also ompanies the formation of cholesteric acid.

Biliary calculi are often found in the gall-bladder in large mbers; they vary a good deal in appearance and shape: in some es they are nearly semi-transparent, and crystallized through- t, at other times they are strongly tinged with the colouring atters of the bile. Occasionally the cholesterin is deposited on a nucleus of phosphate of lime, or of biliary colouring matter combination with lime.

In some species of oriental goats, concretions, called *bezoars*, a brownish-green colour, are occasionally found in the stomach d intestines; they contain a substance termed *lithofellic acid* ($O,C_{40}H_{35}O_{7}$), which a good deal resembles cholesterin in appear- ce. This body crystallizes in six-sided prisms, or in small mbic prisms, with an oblique terminal face. It is insoluble in ter, sparingly soluble in ether, but freely soluble in hot alcohol in acetic acid. Concentrated sulphuric acid also dissolves it ly, the solution becoming milky when diluted with water.

Lithofellic acid fuses at 400°, and if heated to a little beyond this, it is converted into a resinous mass, the fusing point of which is reduced to about 230°. If this resin be redissolved in alcohol it is again converted into the crystallizable acid. Lithofellic acid burns with an agreeable odour and a white smoky flame. It combines with the alkalies and forms soluble salts; the salts of lead and of silver are insoluble, and soften in hot water. Lithofellic acid is distinguished from cholesterin by its higher melting point and by its ready solubility in solutions of the caustic and carbonated alkalies, and in acetic acid. When treated with sulphuric acid and sugar, it gives a violet colour resembling that produced by glycocholic acid.

The following Table will assist in indicating the relations which subsist between the most important of the numerous compounds obtainable from the bile:—

Glycocholic acid	$C_{52}H_{43}NO_{12}$	Hyocholic acid . .	$C_{54}H_{43}NO_{10}$
Cholonic acid .	$C_{52}H_{41}NO_{10}$		
Cholic acid . .	$C_{48}H_{40}\ O_{10}$	Hyocholalic acid .	$C_{50}H_{40}\ O_{8}$
Choloidic acid .	$C_{48}H_{39}\ O_{9}$		
Dyslysin . . .	$C_{48}H_{36}\ O_{6}$	Hyodyslysin . . .	$C_{50}H_{38}\ O_{6}$
Taurocholic acid	$C_{52}H_{45}NO_{14}S_{2}$	Hyocholeic acid .	$C_{54}H_{45}NO_{12}S_{2}$
Cholesterin . .	$C_{52}H_{44}\ O_{2}$	Lithofellic acid . .	$C_{40}H_{36}\ O_{8}$
Taurin . . .	$C_{4}\ H_{7}NO_{6}S_{2}$	Glycocine . . .	$C_{4}\ H_{5}\ NO_{4}$

(1491) *Colouring Matters of the Bile.*—If an alcoholic solution of bile be filtered through a column of animal charcoal, it runs through nearly deprived of colour. The colouring matter of the bile appears to exist in two modifications; one of them is brown, the other green: the latter is abundant in the herbivora; it forms the *biliverdin* of Berzelius, who considers this green pigment to be identical with chlorophyll, or the green colouring matter of vegetables. It is insoluble in water, but is taken up by alcohol and by ether. In human bile the brown pigment preponderates; it has been termed *cholepyrrhin* or *biliphæin*. This brown colouring matter is of an acid character; it is soluble in chloroform, from which it may be obtained in crystals (Brucke). It combines with the alkalies and the earths; with the latter it forms compounds which are insoluble in water and in alcohol. The brown colouring matter of the bile is very rapidly altered by reagents. The changes of colour produced in it by the action of nitric acid have been proposed as one means of detecting the presence of bile in certain cases, as, for instance, when it occurs in urine: when a solution containing this colouring matter is mixed with nitric acid, the colour becomes at first green, then blue, rapidly passing into violet; it then changes to red, and finally the red slowly passes into yellow.

Many biliary calculi contain a large quantity of the colouring rial in combination with lime, with which it forms a brown ound insoluble it water. Calculi are also frequently found in x composed of a pure intense yellow colouring substance, much d by artists for its durability and for the brilliancy of its tint. The greater part of the colouring matter of the bile, with a l portion of bile itself, passes off with the fæces, but by far larger proportion of this secretion is reabsorbed into the m, where it has been conjectured to supply a portion of the rial consumed by the oxygen in respiration for the mainte- e of animal heat. This theory, however, seems to be ques- ble, since the constituents of the bile have not been satisfac- discovered in normal blood.

The resinous acids of the bile, which constitute the charac- ic components of this secretion, appear to be truly formed e liver itself. The mode of action of the liver differs there- in an important manner from that of the kidneys, since these ls do not produce the compounds excreted by them.

(1492) Sugar is not an ingredient in normal bile, but it is rkable that this substance is rapidly formed from one of the tituents of the liver itself, in which organ sugar is found in con- rable quantity after death (Bernard). The full significance of fact, in its physiological bearings, cannot be said to be at ent understood.

In cases of metallic poisoning, the liver has generally been nd to contain traces of the metal that has been exhibited, but important to bear in mind that iron, copper, and manganese always present in minute quantity in the ashes of healthy an bile. Lead, arsenic, and antimony have been detected in liver, in cases where they had been taken in poisonous doses; there is no reason to suppose that if death had occurred ng the exhibition of these metals in medicinal doses, that es of these substances would not be found in the liver, if sought for.

C. *Excrementitious Products.*

(1493) 1. The Urine.—This fluid is separated by the kidneys arterial blood. Human urine, to which the following re- s are applicable, unless otherwise specified, is usually of a amber colour, and, if passed when fasting, is feebly acid to s; but, according to Bence Jones, the acidity diminishes g digestion, and whilst this process is most active, the urine en found to be slightly alkaline. Urine has a peculiar odour, a saline bitter taste. Its specific gravity varies with the

The quantities of the various components of the urine are, however, subject to material variation, even in the same individual at different times, although he may be in perfect health. The quantity of solid matters, and especially of urea, is proportionately increased with the increased amount of exercise taken, as the direct experiments of Lehmann have shown. Indeed it has been found to be a general rule that the waste and reparation of the body are in direct proportion to the amount of exercise taken: during active exercise the number of inspirations in a given space of time is increased, a larger quantity of oxygen is brought into contact with the tissues, and a more rapid waste of their components ensues, and consequently a greater supply of food is demanded after exercise than after the individual has been in a state of repose for an equal interval.

In all animals the urine appears to form the principal outlet for the nitrogen of the effete azotised tissues of the system, though the compounds in which it is excreted vary with the kind of animal. Carnivorous animals, such as the lion, the tiger, and the leopard, excrete the greater part of the nitrogen in the form of urea; and produce but a small quantity of uric acid. The urine of these animals is clear, and nearly colourless, with a strongly acid reaction; but it putrefies rapidly, and quickly becomes alkaline owing to the decomposition of the urea. The herbivora likewise excrete a large quantity of urea; but hippuric acid in considerable quantity is contained in their urine, whilst uric acid is nearly wanting. Many of these animals, such as the rhinoceros and elephant, excrete a urine containing a large quantity of the bicarbonates of lime and magnesia, in consequence of which their urine is either turbid when voided or it speedily becomes so. The phosphates are almost entirely absent from the urine of the herbivora, but they appear abundantly in the fæces of these animals. Carnivorous birds excrete uric acid in abundance in the form of a superurate of ammonia, and they also appear to excrete small quantities of urea: but urea is completely absent in granivorous birds, which excrete abundance of uric acid combined with a variable amount of ammonia. In those carnivorous reptiles which live out of water, such as the serpent tribe, the excretions consist almost entirely of uric acid; while in the amphibia, such as the frog and the toad, urea appears, with very little uric acid. Uric acid has also been found in the excrements of insects. From these facts, it is clear that in those animals which drink freely, the nitrogen is excreted principally in the form of urea, while in those which take very little fluid nutriment it is separated chiefly in the form of uric acid.

In diseases attended with fever the quantity of uric acid in human urine is greatly increased. The question of the source whence uric acid is derived is full of interest, especially to the practical physician, since its morbid prevalence is intimately connected with some of the most distressing maladies which afflict the human frame, such, for example, as gout, rheumatism, and certain forms of calculous concretions from the urine. In some kinds of gout, uric acid is developed and retained in the system, chiefly in the form of urate of soda, in the neighbourhood of the smaller joints, such as those of the fingers and toes and the wrists, forming deposits commonly known as chalk-stones. The system is in these cases loaded with lactic and acetic acids, the latter of which is thrown off abundantly in acid sweatings. Dr. Garrod, in cases of gout, has invariably found uric acid to be present in the blood, and he has also frequently detected it in the blood in Bright's disease: it has been found occasionally in healthy blood. Uric acid is likewise discovered without difficulty in the blood of animals from which the kidneys have been extirpated.

The constitution of the urine is found to vary at different times of the day. That voided in the morning, for example, after the lapse of a considerable interval without the ingestion of food, is the result chiefly of chemical actions going on within the body itself, and is furnished by the decomposition of the tissues. Such urine has a very different composition from that passed in the evening, into which various bodies have been absorbed directly from the stomach. The nature of these bodies necessarily varies with that of the food, which also materially influences the quantity both of uric acid and of urea. With reference to this point, it was found by Lehmann in a series of experiments upon his own person, that after restricting himself to an animal diet for several days, he excreted daily 821 grains of urea, and 21·6 grains of uric acid. After an exclusively vegetable diet for a similar period, the quantity of urea in twenty-four hours amounted to 348 grains, and the uric acid to 15·4 grains; and after subjecting himself to a diet from which nitrogen was as far as possible excluded, the quantity of urea fell to 237 grains. When a highly azotised diet was taken, the same observer found that five-sixths of the entire quantity of nitrogen taken in the food was eliminated from the system in the form of urea. With an ordinary mixed diet the urine amounted to 37·3 ounces daily, and it contained 501 grains of urea and 18·2 of uric acid. These quantities of urea and uric acid are somewhat higher than the average of those excreted by the healthy adult. The quantity of sulphuric acid in the urine is also mainly influenced by the proportion of azotised food taken; this acid indeed appears to be derived principally from the sulphur contained in the albuminoid compounds assimilated from the food. When a mixed diet was used, Lehmann found the quantity of sulphuric acid excreted daily to amount to 108 grains; with an animal diet it rose as high as 165 grains, and when a purely vegetable diet was consumed, the quantity of sulphuric acid excreted in the twenty-four hours fell to 90 grains. Many substances when taken into the stomach pass off unchanged by the kidneys, especially those which are of a saline nature, such, for instance, as iodide of potassium, and ferrocyanide of potassium: these salts may be commonly detected in the urine within half an hour after they have been swallowed.

(1494) *Urinary Concretions.*—Although the urine in a healthy individual usually remains clear and transparent, even after it has cooled, it not unfrequently, under the influence of disturbed health, deposits more or less abundantly some of its less soluble constituents: these deposits in some cases assume the form of a light flocculent powder; at other times they appear in more compact grains, which constitute the different forms of gravel, and in other instances they collect into larger masses, and give rise to urinary calculi.

The most common urinary sediments are those which contain uric acid. When the uric acid is uncombined with bases, it often appears in small crystalline masses resembling grains of coarse sand, constituting the ordinary variety of *red gravel*, which consists of uric acid tinged with the yellow colouring matter of the urine: this sediment, if examined under the microscope, is usually seen to possess the form of rhomboidal crystalline plates, the edges of which are frequently rounded. In other cases the acid is found in the form of a light-brown amorphous sediment consisting of urates of soda and ammonia. Both these sediments, and especially the latter, are materially influenced by diet: excess of any kind, particularly in animal diet, drinking too much of acescent fermented liquors, over-anxiety, exposure to cold, damp weather, and want of exercise, very frequently produce an increased excretion of uric acid, and cause a deposit of the urates of soda and of ammonia even from persons in health. In those suffering from a habitual deposit of red gravel, an animal diet frequently aggravates the disease in a remarkable manner. On the other hand it has been observed that uric acid is less abundant in the urine in summer, and is generally diminished after copious sweats. Lehmann states that the formation of uric acid calculi is unknown in tropical climates.

When *phosphoric acid* is present in the urine in excess, it sometimes shows itself in the form of a white sand, which is usually crystallized, and consists of phosphate of magnesia and ammonia: but occasionally the deposit is amorphous. These two varieties of sediment constitute *white gravel;* they are attended almost constantly by an alkaline state of the urine.

The principal varieties of urinary *calculi* as distinguished from *sediments* are the following:—1. Uric acid; 2. Urate of ammonia; 3. Oxalate of lime; 4. Phosphate of lime; 5. Phosphate of magnesia and ammonia; 6. Fusible calculus (a mixture of the two preceding ones); 7. Xanthic oxide or Xanthine; and 8. Cystic oxide. Urinary calculi are in many cases formed upon some foreign body as a nucleus, such as a clot of blood or a crystal of any kind.

1. *Uric acid* calculi are usually of a brownish-red or fawn colour: they have a smooth or finely tuberculated surface; when sawn through they are generally found to be composed of concentric laminæ, and are somewhat crystalline. If a fragment of such a calculus be heated before the blowpipe, it is consumed, emitting a peculiar animal odour, and leaving only a minute white ash. This variety of calculus is soluble in a solution of potash, and uric acid is precipitated in white silky crystals on supersaturating the solution with an acid. If a fragment be heated on a slip of glass with nitric acid, it is dissolved with effervescence, leaving an orange-coloured residue, which is rendered of a beautiful pink or crimson by the addition of a drop of ammonia, after which the addition of a solution of potash developes a magnificent purple.

2. The *urate of ammonia* calculus is very rare: it is usually clay-coloured, and smooth; and is deposited in fine concentric layers of an earthy appearance. It is more soluble in water than the preceding variety, and is dissolved with extrication of ammonia when heated with a solution of potash; in other characters it resembles uric acid.

3. *Oxalate of lime* often occurs as a morbid ingredient of urine. The *mulberry calculus* consists of this substance: this form of concretion has usually a deep brown colour; it is deeply tuberculated and rough, and is very dense and hard. When heated before the blowpipe, it first blackens, and then, if exposed to a moderate red heat, it burns to a white ash consisting of carbonate of lime, which is dissolved by acids with effervescence; but if it has been more strongly heated, the ash is alkaline to test-paper,

sists of pure lime. The finely powdered calculus is soluble c and hydrochloric acids, but it is insoluble in acetic acid. tions of oxalate of lime have been found in some of the nimals, as well as in man. Prout considered its occur- in the urine to be due to faulty assimilation of saccharine , but the conditions under which it is produced are not certained.

Phosphoric acid when combined with lime forms a rare of calculus, the *bone earth calculus* ($3\,CaO,PO_5$) which is of a pale brown colour with a very smooth surface, and is ly laminated in its texture; these laminæ are often deposited tals radiating from the nucleus. The bone earth calculus sible before the blowpipe; it is readily dissolved by hydro- acid, and the phosphate of lime may be precipitated from lution in a gelatinous state by the addition of ammonia.

Another form of phosphatic calculus consists of the phos- f magnesia and ammonia ($H_4NO, 2\,MgO,PO_5$). It is not uent, and is spoken of by the older writers as *triple phosphate.* hite, brittle, and more or less crystalline in structure; it is laminated, and its surface is uneven. It fuses with difficulty the blowpipe, emitting an odour of ammonia: dilute acids e it readily, and the solution when neutralized with ammonia s it again in a crystalline form.

A third species of phosphatic concretion is the *fusible calculus,* consists of a mixture of the two preceding varieties. It is of t occurrence, and forms white friable masses which are rarely ted, and often acquire a large size. This form of calculus eadily before the blowpipe; it is soluble in dilute acids, from oxalate of ammonia separates lime, and pure ammonia throws phosphate of magnesia. When the occurrence of phosphatic ts is habitual, it always indicates a state of constitution y disordered. Occasionally these phosphates are secreted he lining membrane of the bladder in large quantity, forming tar-like mass of concretions. The earthy phosphates are uced into the system in considerable quantity in the seeds of ealia: beer contains so much phosphate of magnesia, that, on ammonia, the double phosphate of ammonia and magnesia ipitated in abundance.

e phosphates are also common ingredients of calculi in rous animals: in many instances they appear to be deposited he urine simply from the development of free alkali, either to the decomposition of the urea, or to excess of alkaline introduced *from without.*

Compound calculi are not unfrequent; they are formed of a succession of laminæ, composed of one or other of the foregoing varieties. For instance, uric acid, oxalate of lime, and fusible calculus sometimes occur in successive layers in the same calculus.

7 and 8. The characters of the rare calculi containing the compounds known as *xanthic* and as *cystic oxide* have been already described (1422, 1443).

The further prosecution of this subject belongs more properly to a work devoted to pathology than to one treating of general chemistry. For the microscopic appearances of the various substances deposited from the urine, the reader is referred to Golding Bird's treatise on urinary deposits, and to Beale's treatise on the microscope.

(1495) The urine in disease undergoes other important modifications in its constitution: two only of these will be adverted to on the present occasion.

Diabetic Urine.—In the disease termed *diabetes* the urine is found to contain a large quantity of grape sugar, which is almost entirely wanting in the healthy state of the secretion. The source of this sugar lies in the faulty digestion of the food. The sugar appears to be absorbed directly from the alimentary canal into the blood, and is thence separated unchanged by the kidney. Dr. Percy has found that sugar when injected into the blood is separated in an unaltered form in the urine. The quantity of sugar which is excreted in twenty-four hours by patients suffering from diabetes is frequently enormous, amounting in some cases to upwards of 1¼lb. of solid glucose. The proportion of sugar excreted in this disease is greatly under the control of the diet; substances which contain much amylaceous or saccharine matters, such as bread and potatoes, always occasion the excretion of a larger quantity of sugar: under the use of opium, and an animal diet, the saccharine matter is very considerably diminished.

If sugar be suspected in the urine, its presence may be inferred by the employment of Trommer's test, in which the reducing action of glucose upon the salts of copper is taken advantage of. The urine is first rendered strongly alkaline by the addition of a solution of potash, and a few drops of sulphate of copper in solution are added; on agitation, the hydrated oxide of copper, which is at first precipitated, is redissolved; and upon boiling the liquid, the yellow hydrated suboxide of copper, which is speedily converted into the red anhydrous suboxide, is thrown down. If this reaction does not occur, no sugar is present. Since, however, other bodies besides

exercise a similar reducing influence on the oxide of copper,
resence of sugar should be further confirmed by the test of
ntation. In order to apply this test, a small quantity of
is added to a portion of the urine, which is placed in an
ted tube over mercury, and exposed to a temperature of 80°;
gar be present, carbonic acid gas is liberated in the course of
hours. Bence Jones, however, finds minute quantities of
r even in healthy urine (*Q. J. Chem. Soc.* xiv. 40) in quan-
varying from 1·1 to 1·9 grs. per 10,000 grs. of urine.

lbuminous Urine.—The other important alteration of the
e here to be noticed consists in the excretion of a large quan-
of albumen. When this occurs, it may be recognised by
tly acidulating the urine, and applying heat. Coagulation
ws if albumen be present; and a similar effect is produced on
ddition of nitric acid. In this disease the seat of mischief is
kidney itself, and its powers of secretion are modified in an
rtant manner. In a state of health, this organ does not
the albuminous portion of the blood to escape, but in par-
ar forms of disease it permits albumen to pass, and retains
rea, which may then be detected in dropsical effusions, and
rious fluids contained in the body.

(1496) 2. CUTANEOUS EXCRETIONS.—Notwithstanding the
importance to health of the due performance of the functions
e skin as an excretory organ, the chemical nature of the pro-
which it throws off has been but imperfectly studied, since the
ction of these compounds is attended with considerable diffi-
, owing partly to the great extent of surface from which the
tion takes place, and partly to the variation in composition
h it presents in different parts of the body.

The solid not volatile constituents of the sweat have been
d to range between about 0·5 and 1·25 per cent.; the pro-
ion of water varying with the temperature and hygroscopic
lition of the atmosphere, with the amount of liquids swallowed,
the kind of exercise taken by the individual, and with the
lity of the circulation. Among the solid constituents, chloride
odium is the most abundant. Lactates, butyrates, and acetates
mmonia and soda are also present, besides small quantities of
phate of lime; phosphates of the alkalies are absent, and the
hates are found only in very small amount. Carbonic acid and
ogen are likewise exhaled from the surface of the body in con-
rable quantity, particularly the former. The sweat contains also
antity of a *peculiar azotised* matter, very prone to decomposi-

tion, as well as an odorous principle. The cutaneous excretion from the general surface of the body has almost invariably an acid reaction, owing to the presence of free lactic acid; but the excretion from the axillæ and the feet is sometimes found to be alkaline. With regard to the quantity, all that can be stated is that it usually exceeds in bulk that of the urine during the summer; but that in winter the urine preponderates in amount, while the quantity of cutaneous transpiration is greatly and proportionately diminished. In fact, processes occur upon the surface of the skin, which resemble those both of the kidney and of the lungs: thus, like the kidneys, the skin excretes nitrogen and acid substances as well as the chlorides; and, like the lungs, it separates large quantities of carbonic acid and aqueous vapour. The actions of the skin, and of the kidneys and lungs, are, therefore, though to a very limited extent, vicarious; and when the functions of the skin are seriously interfered with, it usually happens that derangements more or less serious, either of the kidneys or of the lungs, occur.

(1497) 3. Solid Excrements.—After the chyle has been absorbed into the system during the gradual passage of the mixed constituents of the food through the intestinal canal, those parts which are destined to become excrementitious gradually acquire a fæcal odour, and are at length ejected from the body. The composition of these excrementitious matters necessarily exhibits great variations, which depend mainly upon the nature of the food taken. Berzelius found a specimen of human excrement which he examined, after the use of an ordinary mixed diet, to contain three-fourths of its weight of water, the rest consisting of biliary matter and alimentary débris. A large quantity of phosphates of lime and of magnesia, and other insoluble salts of the food, are obtained on incinerating the dried residue. Playfair found in a sample which he examined, about 15 per cent. of nitrogen in the dry residue, and 45 per cent. of carbon. The ratio which these numbers bear to each other does not differ much from that which represents the proportion of the same elements in fresh muscle, which likewise contains three-fourths its weight of water. According to Liebig, the total average weight of fæculent matter in its recent state excreted by a healthy adult in twenty-four hours amounts to $5\frac{1}{2}$ ounces. The offensive odour of fæcal matter is due to some intermediate products of oxidation. These odorous substances have not been accurately examined, but they may be produced artificially by fusing casein with hydrate of potash, as in the preparation of tyrosine (1428). This odour is of a different nature and of re putrid character when the quantity of bile secreted is below sual amount.

r. W. Marcet has obtained from healthy human excrement, uliar crystallizable principle which, from its origin, he terms *etine;* he attributes to it the formula $C_{78}H_{78}SO_2$: it has a y alkaline reaction; it fuses at a little above 200°, and is luble in water and in a solution of potash, but is readily ble in ether. He has also extracted from the excrements a ble olive-coloured fatty body termed *excretolic acid;* but has recorded any attempt to determine its composition.

(1498) 4. Pus.—This is a liquid which is never met with pting as a product resulting from actions excited by injury, or isease. When the suppurative process is going on favourably, forms a thick, opaque, yellowish fluid, which, when examined he microscope, is found to consist of a transparent liquid, in h a large number of corpuscles are seen to be floating. These uscles are larger than the red corpuscles in human blood; they ist of a granular cell membrane enclosing a viscid granular er, and a nucleus which adheres to the membrane. Pus rally has a feebly alkaline reaction. The fluid portion holds a iderable quantity of albumen in solution, and closely resembles ary serum: leucin is also commonly present (Bödeker). pus globules contain a large proportion of fat, and of choles- . *Pyin* is the name which has been given to an albuminoid ance sometimes found in pus; it is soluble in water, but is pitated by acetic acid and by a solution of alum. The dried ue of pus yields a large amount of salts; in the experiments ehmann the saline constituents exceeded 12 per cent. of the dry matter: the proportion of phosphates and of salts of sh was very considerable.

CHAPTER XIII.

ON THE NUTRITION OF PLANTS AND ANIMALS.

§ I. *On the Nutrition of Vegetables.*

1499) Organized beings have been arranged under the two divisions of *plants* and *animals;* and although the lowest a in each *division approximate* so closely that it is difficult to decide where one division begins and the other ends, yet in their general relations they are not only widely different, but even opposed to each other in the functions which they discharge in the economy of creation, the operations of the plant being complementary to those of the animal in the nicely adjusted balance of organic life, each affording support and nutriment to the other. The principal functions of the plant and animal may be contrasted thus :—

Plants	*Animals*
Decompose water and carbonic acid.	Produce and evolve water and carbonic acid.
They evolve oxygen.	They absorb oxygen.
They absorb and assimilate nitric acid and ammonia.	They produce and emit urea, and other azotised compounds which yield ammonia.
They are fixed in the soil.	They possess the power of locomotion.
They have no power of voluntary action.	Their actions are under the control of the will.
Their growth is continuous, and there is no absorption of matter once deposited.	Their growth, and the absorption of deposited matter in the adult, go on *pari passu*.

Two important functions have been allotted to the vegetable creation, one of which consists in the elaboration from inorganic matter of the various materials necessary to the support of animal life; the other consists in the removal of carbonic acid from the atmosphere, the plant retaining the carbon and fixing it in its tissues, whilst the oxygen is restored to the air. These wonderful changes are produced by the actions of the vegetable cell; each cell possessing a separate and independent power, by means of which it is enabled to assimilate new matter; from this assimilated matter it produces new cells, and these in like manner multiply and produce innumerable other cells. These successive developments of vegetable cells may be readily watched under the microscope in the case of the growth of the globules of yeast (964). The compounds produced in the yeast globules are cellulin, which forms the cell membrane, and the internal substance, which contains a body allied to albumen. The plant-cell in the case of yeast does not elaborate the azotised product, but assimilates it from the solution in which it grows; there is, however, no doubt that albumen is elaborated in other instances by the vegetable cell:—in the wheat plant, for example, the azotised gluten is stored up in the seed, and in this case it can only be derived from the inorganic materials of the soil and of the atmosphere.

But the mere existence of an organized structure, even when animated by the vital force, is not sufficient to produce these results of vital activity. It is necessary, in addition, that the plant be exposed to a temperature ranging between 40° and 90°, and to a certain degree of moisture. In the higher manifestations of plant life, solar light is also essential. If at any time the temperature fall so low that the plant is frozen, its vitality is destroyed, and the delicate structures of the tissues are impaired by the solidification and forcible expansion of the juices which they contain. Life is also destroyed not less completely by exposure of the organism to a temperature of 212°, or even to one considerably below that point. The higher orders of plants require for their full development that they shall be rooted in a congenial soil, and be supplied freely with air and moisture.

A plant in a state of health is continually undergoing increase: this increase, however, may either be checked or facilitated by modifying the circumstances under which it is placed. In order that the method of regulating this development may be more fully understood, it is necessary to examine what the materials are of which this increase consists, and whence they are supplied. In all plants there are two distinct sets of substances present; one of these is organic in its nature and is represented by sugar, starch, wood, albumen, &c.; the other is inorganic, and is represented by the various salts found in the ashes of plants. The materials from which these compounds are formed must, therefore, be supplied in some shape or other to the growing plant; in fact, they constitute its food. Experiment has, however, proved that the form in which these matters are presented to the plant is by no means unimportant, for the elementary bodies, with the exception of oxygen, are never directly assimilated; they must previously have entered into combination in some form or other. The compound constituents of the food of plants are supplied from two sources, the atmosphere and the soil. Those furnished by the atmosphere consist chiefly of carbonic acid, water, ammonia, and nitric acid; while the saline compounds, which vary with the nature of the plant, are derived from the soil: without these different articles of food—viz., carbonic acid, water, ammonia, and the salts of the soil—plants could no more continue to exist than animals could do if deprived of their natural nutriment.

The root of a plant may be considered as its mouth, and the leaves as its lungs. When a shower of rain descends through the air, it carries with it all the soluble matters which that portion of the air contains; these soluble matters consist chiefly of carbonic acid, with minute quantities of carbonate and nitrate of ammonia. The carbonic acid, as we have already stated, is abundantly furnished by the processes of respiration in animals, by combustion, and by a variety of other sources. The ammonia is furnished mainly by the putrefaction and partial oxidation of animal and vegetable matters, and is present in the air, in a quantity far more minute than carbonic acid, but still in appreciable amount (311). Nitric acid is produced whenever a flash of lightning passes through the moist air, and this compound is generated even when silent discharges of electricity take place. Every shower of rain which falls to the earth, thus dissolves and carries with it food for vegetation; charged with these nutritive materials, the water percolates through the soil, from which it takes up small quantities of soluble salts. It thus arrives at the spongioles of the roots, where it is absorbed and carried up by the ascending current of sap, to the leaves, and to the remotest extremities of the branches,* where, under the influence of some azotised matter, and of the solar light, the carbonic acid undergoes a remarkable change: a portion of the water likewise experiences decomposition, in consequence of which, oxygen gas, mingled with a quantity of nitrogen varying from one-half to one-tenth of the bulk of the oxygen, is given out. Supposing that this decomposition be effected upon carbonic acid and water, in the proportion of one equivalent of each of these compounds, a substance would be formed, having the same ultimate composition as fructose, or fruit-sugar; $C_2O_4 + H_2O_2 - O_4 = 2\,CHO$, or $6\,(C_2O_4 + H_2O_2 - O_4) = C_{12}H_{12}O_{12}$.

Sugar, indeed, appears to be the basis or foundation of organic matter in general, and from it all the varieties of organized products might be obtained, by the addition or subtraction of water, oxygen, and ammonia. If fructose ($C_{12}H_{12}O_{12}$) be deprived in the plant of 2 equivalents of water, starch or cellulin is the result, and starch may again be brought into solution when necessary for the plant, by the action of diastase, or of some principle which acts as a ferment, and enables it to resume the water which it had lost. The latter change actually takes place during the germination of seeds, which, when moistened, swell and absorb oxygen, whilst carbonic acid is emitted, and the starch, under the influence of diastase is converted into sugar, in which form it serves as food for the young plant. If the growth of the seed be checked at a particular stage by suddenly raising the temperature, the greater part of the starch will be found to have disappeared from the seed, and its place will have been taken by sugar; these being in fact the changes which occur in the process of *malting* (949). But, if germination be allowed to proceed, the starch and the sugar gradually disappear, and ligneous fibre is formed, which contains the elements of fruit-sugar minus 2 equivalents of water. During the ripening of fruits the pulp gradually assumes water, and becomes sweet; the fibrous portions of the fruit being greatly diminished, while the saccharine and mucilaginous constituents are increased.*

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* Although it has been stated that the principal supply of carbonic acid is furnished to the plant as a solution in water which is absorbed from the soil by the roots, it must not be forgotten that the leaves also present powerfully absorbent surfaces, and, like the lungs in animals, not only minister to the respiration of the organism, but are frequently the inlet of a variety of substances which are capable of assimilation, as well as of those that are not so. Carbonic acid, in particular, is absorbed by the leaves with great rapidity, as has been shown by the experiments of Pepys and others.

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* According to the observations of Fremy and Decaisne, most unripe fruits contain starch (but this appears to be incorrect as a general rule), ligneous fibre, pectose (953), and a peculiar substance capable of furnishing gum, which they have termed *gummose:* in addition to these ingredients, tannin and some of the vegetable acids are present. During the period of the growth of the fruit, whilst it retains its green colour, it decomposes carbonic acid, and emits oxygen like the leaves of a tree: but when the fruit begins to ripen it gradually becomes softer and more transparent, and oxygen is absorbed, whilst carbonic acid is evolved. During this evolution of carbonic acid, a succession of slow oxidations is taking place within the cellules of the fruit; the tannin first disappears, and the vegetable acids are then gradually consumed; when this point has been reached, the fruit is generally in the proper condition to be eaten. If it be kept longer, the sugar in its turn experiences oxidation, and the fruit becomes flat and tasteless, and by prolonged keeping it undergoes decay.

The correctness of most of the foregoing statements is easily verified. The process of ripening generally takes place best whilst the fruit hangs upon the tree, but in many cases, as in the apple, the pear, and the orange, the fruit continues to ripen after it has been gathered. In each case oxygen gas is absorbed, and carbonic acid evolved. The proportion of acid contained both in growing and in detached fruits is less in the ripe than in the unripe fruit. The disappearance of the acidity in fruits during the process of maturation appears to be dependent upon this absorption of oxygen, as is well exemplified in the case of the common cyder-apple. This fruit, when whole, has an austere sour taste, but, by crushing and exposing it to air for a short time, the flavour becomes sweet and agreeable; the vegetable acid having undergone a slow oxidation, in consequence of which it has become converted into carbonic acid. The increase in the quantity of sugar during ripening is in some cases very great, as for instance in the apricot, which whilst green contains scarcely any sugar, though in the ripe fruit as much as 10 or 11 per cent. has been found.

Buignet (*Ann. de Chimie*, III. lxi. 233) has submitted a large number of fruits to a careful examination during the process of ripening. He finds that in acid fruits the sugar either consists of inverted sugar, as in the grape, the cherry, the gooseberry, and the fig, or it consists of a mixture of this sugar with pure cane-sugar, as is the case in the apricot, the peach, the apple, the pine-apple, the citron, the orange, the plum, and the raspberry. This inverted sugar appears to have been derived from cane sugar, as no other variety of sugar appears to be convertible into it. The banana is not an acid fruit; it contains a good deal of starch during ripening, and yields sucrose.

The cane-sugar of acidulous fruits, however, does not appear to be derived from starch—indeed, no starch is to be found in any of these acid fruits; but instead of starch they contain an astringent compound which furnishes a colour-

It may be instructive to observe how readily, by absorption of oxygen and separation of water from sugar, the principal vegetable acids may be supposed to be generated :—

$$(1)\quad 2\,(\overbrace{3\,HO,C_{12}H_5O_{11}}^{\text{Citric acid.}}) = 2\,\overbrace{C_{12}H_{12}O_{12}}^{\text{Glucose.}} + 3\,O_4 - 4\,H_2O_2\,;$$

$$(2)\quad 6\,(\overbrace{2\,HO,C_4O_6}^{\text{Oxalic acid.}}) = 2\,\overbrace{C_{12}H_{12}O_{12}} + 9\,O_4 - 6\,H_2O_2\,;$$

$$(3)\quad 3\,(\overbrace{2\,HO,C_8H_4O_8}^{\text{Malic acid.}}) = 2\,\overbrace{C_{12}H_{12}O_{12}} + 3\,O_4 - 3\,H_2O_2\,;$$

$$(4)\quad 6\,(\overbrace{2\,HO,C_8H_4O_{10}}^{\text{Tartaric acid.}}) = 4\,\overbrace{C_{12}H_{12}O_{12}} + 9\,O_4 - 6\,H_2O_2.$$

Again, if instead of forming sugar, 10 atoms of carbonic acid, and 16 equivalents of water were to give up the whole of their 56 equivalents of oxygen, a compound would be furnished, corresponding to oil of turpentine, and forming the basis of many of the resins; $10\,C_2O_4 + 8\,H_2O_2 - 14\,O_4 = C_{20}H_{16}$.

The complicated azotised principles may be also traced in theory to grape-sugar; thus :—

$$12\,\overbrace{C_{12}H_{12}O_{12}}^{\text{Fructose.}} + 16\,H_3N = 4\,\overbrace{C_{36}H_{27}N_4O_{12}}^{\text{Protein.}} + 42\,H_2O_2 + 3\,O_4.$$

These equations have been given with the view of pointing out the simple relations of sugar to the various organic acids, and not with any intention of asserting that the changes which they indicate actually take place in the form thus represented, though it is obvious that some such changes must occur. Sugar or gum,

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less combination with iodine, and which has a still stronger tendency to unite with iodine than is possessed by starch itself. This circumstance may be taken advantage of in determining the relative quantity of this substance present in a given fruit, or in the same fruit at different periods of maturity; for by employing a standard solution of iodine and adding starch paste to the liquid, it is easy to ascertain the number of divisions of the iodine liquor added from the burette before the starch begins to show its characteristic coloration; the compound formed contains from 16 to 17 per cent. of iodine. When this astringent substance is boiled with diluted sulphuric acid (1 of acid to 100 of water) it yields a saccharine solution.

Buignet considers that the conversion of the cane-sugar into inverted sugar in the fruit is due to a special ferment, not to the action of the acid: the following experiment supports this view :—He took two portions of peach juice, diluted one with twice its bulk of alcohol, by which the ferment was coagulated and rendered inert; the other portion he mixed with twice its bulk of water containing carbonate of lime in suspension; in half an hour he filtered both liquids; the rotatory power of each was alike; in twenty-four hours the neutralized liquid, containing unaltered ferment, had become ropy, and the whole of the cane-sugar had become inverted, while the portion to which the alcohol had been added remained unaltered.

and starch or ligneous fibre, are amongst the most abundant and generally diffused vegetable productions, and it is very probable that these bodies may furnish the materials from which the various vegetable acids and other simpler compounds of vegetable origin are obtained: but if this hypothesis be doubted, there is no difficulty in tracing these acids and the other bodies to the carbonic acid and water upon which the plant operates. For instance, oxalic acid might be produced from carbonic acid and water by the following changes; $4\,C_2O_4 + 2\,H_2O_2 - O_4 = 2\,(2\,HO, C_4O_6)$. In the case of malic acid, the changes might be the following: $4\,C_2O_4 + 3\,H_2O_2 - 3\,O_4 = 2\,HO,C_8H_4O_8$; and so on with the others.

It is impossible in the existing state of our knowledge, to trace the cause, or even the exact nature, of the changes produced in the various fluids which circulate in the plant or in the animal. The theory which has the strongest apparent analogies in its favour is, that, by the presence of some albuminous ferment analogous to diastase or to synaptase, an elimination of various compounds takes place in particular organs, just at those points where these ferments are deposited. It is further supposed that the same complex organic fluid is capable of undergoing changes differing with the nature of the substance which excites fermentation, and that hence it happens, that the same fluid may deposit in different tissues secretions possessed of very different qualities (948). The substances thus produced must necessarily be complementary to each other: that is to say, the product of secretion and the altered fluid which furnishes it, taken together, must contain the same elements as the original substance from which they were produced. The foregoing hypothesis affords no explanation of the manner in which compounds previously existing in the circulating fluid, as urea is known to do in the blood, are separated from it by the ordinary operation of secretion, but the processes of diffusion and osmosis are probably importantly concerned in these cases.

(1500) *Food of Plants.*—As has been already stated, plants are the grand reducing instruments in the great laboratory of Nature, and by renewing to man fresh materials suitable for fuel, they are restoring to him the power which he has exhausted in combustion under the boilers of the steam-engine, or in muscular energy, either in his own person or in that of the beasts subservient to his will. This energy can only be again renewed by a fresh supply of food, which must be drawn ultimately from the vegetable creation. Owing to their reducing action upon water and carbonic acid, plants are continually exhaling oxygen during the day-time, but at night they emit carbonic acid. This emission of carbonic acid appears to be in most instances a mere transudation; the gas is absorbed by the roots by night as well as by day, but in the absence of solar light, neither carbonic acid nor water is decomposed, and both escape unchanged into the air; hence it was at one time supposed that plants during the night actually produced carbonic acid. A real generation of carbonic acid does however take place during the germination of the seed, during flowering, and during the maturation of the fruit; that is to say, at such times as the saccharine or acid compounds are undergoing oxidation. It is worthy of remark, that at this time sugar disappears rapidly from the plant, so that if the sugar-cane or beet-root be gathered after flowering, the produce of sugar is greatly diminished.

The functions of ammonia in vegetation are almost as important as those of carbonic acid, inasmuch as the juices of all plants contain a portion of azotised matters which are necessary to their well-being, and which form an important item in their composition, particularly when considered in relation to the nutritive qualities of the plant as an article of food. One of the principal circumstances which give to animal manure its high value, is the large proportion of ammoniacal compounds which it is capable of supplying.

All plants, in addition to their principal constituents, carbon, hydrogen, oxygen, and nitrogen, contain minute quantities of certain salts, which are no less essential to their growth and development, than those elements which occur in larger quantities. Some idea of the probable use of these inorganic matters may be formed from a consideration of the effects producible in the laboratory, upon the various products of vegetation, by the acids, and by the alkalies. Starch and cane-sugar, for example, are converted into grape-sugar by the action of dilute sulphuric acid aided by heat; and if starch be mixed with dilute sulphuric acid, and with a material which, like peroxide of manganese, furnishes oxygen, formic acid is one of the products. In like manner, under the influence of potash, the natural fats and oils are decomposed into fatty acids and glycerin. Analogous changes may be supposed to occur under the influence of acids and of alkalies, in the yet more subtle chemical operations which are constantly occurring in the organs of living plants and animals, by which the arrangement of their components is modified and altered. In other cases, the obvious use of the saline matters is to furnish a skeleton or support for the plant. This is clearly the principal use of silica in the stem of the grass-tribe, and of oxalate of lime in many of the lichens.

It has already been remarked that the food of plants is derived from two sources, viz., the atmosphere and the soil. From the atmosphere, carbonic and nitric acids, ammonia, and water are supplied; whilst from the soil are furnished the various saline materials necessary to the healthy growth of the plant. Now, in certain cases, all these materials, with the exception generally of carbonic acid and water, may be present in quantity too scanty to produce a luxuriant crop; and the great practical problem submitted to the farmer for solution is the discovery of the nature of the missing materials in any given case; and of the means by which these missing materials may be most cheaply and effectually supplied.

When a crop is carried off from the land, it necessarily takes with it a certain amount of mineral matters. If these mineral bodies be present in the soil in small quantity, and if fresh crops be continually carried off without provision for the return of the matters so removed, the land will in process of time become exhausted of one or more of these necessary ingredients, and sterility will be the inevitable result. One great object of the farmer in manuring his land is to restore these sparingly distributed but essential saline bodies in proportion as they are removed from the farm in the form of corn, of straw, of hay, or of stock which has been reared upon the produce of the land.

It is manifest that a fertile soil should retain its fertility if the manure supplied restore exactly those substances which previous crops had removed. There are few substances which more nearly fulfil this purpose than farm-yard manure; because the salts and mineral ingredients present in the food, pass off almost wholly into the excretions of the animal; and thus the ingredients restored, so far as the supply extends, are nearly identical with those which have been removed: since, if the ash obtained from a given weight of any specific crop be compared with the ash obtained by burning the excreta of animals fed upon an equal quantity of the same crop, the composition of the ash in the two cases will be nearly identical.

It is, however, well known, that the recent droppings of cattle are far more effectual as manure, than the ashes of such manure when burned; partly, because the recent manure contains carbon in a form which, during its decay within the soil, gradually supplies carbonic acid to the roots of the plant; but chiefly, as it appears, because it contains a large proportion of nitrogen, which, during its putrefaction, furnishes ammonia, or some other azotised compound, in a form suited to the wants of the growing crop.

It is owing to similar causes that night-soil and urine possess so high a value as manure. They are much richer in nitrogenized compounds, and in phosphates, than farm-yard manure; and indeed, they contain all the saline constituents of the corn and animal food, as well as almost all the nitrogen of the azotised constituents of the food which had been conveyed into the stomach, whether those azotised constituents had been assimilated or not. The Chinese have long been aware of the importance of these materials as manure, and they collect and carefully restore to their fields that which we in the pride of superior civilization discharge into sewers, and wastefully consign to the ocean, after allowing it to accumulate in offensive mud-banks within our tidal rivers, upon the shores of which, by the ebb and flow of the tide, it is alternately exposed to the heat of the sun and to the action of the water, under circumstances the most favourable to its decomposition, in consequence of which it is constantly contaminating the atmosphere of our large towns with its sickening effluvia.

(1501) *Varieties of Soil.*—In order to render the chemical action of manures intelligible, it will be necessary to take a rapid survey of the principal kinds of soil, and of the nature of the saline ingredients required by ordinary farm crops during their growth.

Soils vary greatly in physical characters, as well as in chemical composition. A soil may, for example, be described as *sandy*, *clayey*, *marly*, or *calcareous*, according as silica, alumina, or lime is the prevailing ingredient. The land will also be *porous* or *stiff*, *moist* or *dry*, partly owing to these peculiarities, and partly owing to its geological position, according as it rests upon sand, upon chalk, upon gravel, or upon clay; its character will also vary, partly owing to its site, according as it lies high or low, and as its surface is inclined or horizontal. But these considerations, though of high importance to the agriculturist, lie beyond the province of the chemist, whose principal attention must primarily be directed to the *chemical* peculiarities of the soil. In order that a soil be fertile it must not only be well drained and sufficiently watered, but it must possess a certain quantity both of organic and of saline ingredients.

Seeds, it is true, in some cases may be made to germinate and develope plants upon flannel, or in well-washed siliceous sand, if duly moistened from time to time with distilled water.

plants thus obtained may even sometimes flower; but they r produce fertile seed; and, if these plants be burned, the ht of the ash which they yield never exceeds that of the ash led by a quantity of seed equal to that from which the plants raised. By adding suitable saline mixtures to washed siliceous l, Wiegmann and Polstorf, however, obtained tobacco, oats, ey, and other plants, in healthy growth, which furnished perfect . In these cases the plants had been supplied with those erials, the absence of which had in the previous experiments ented their mature development. It must not, however, be ily concluded from these results, that organic manures can antageously be dispensed with in agriculture; experience has y proved that a judicious combination both of organic and of ne manures is essential, and it is owing to ignorance of this t that many of the patent mineral manures, when used alone, re so signally failed.

Different classes of plants, in order to the production of a uriant growth, require a soil possessed of physical qualities ich must vary according to the kind of crop; and, in addition this, each species of plant requires a variation in the chemical mposition of the soil, suited to its peculiar habits. The vailing and most abundant components of the soil, whether y be siliceous, aluminous, or calcareous, are not those which rt the greatest influence upon the development of the plant. ey simply constitute the matrix in which the plant grows; and matrix is more or less favourable to its growth according as physical character is more or less conformed to the wants of plant; but the chemically active constituents of the soil conof certain soluble saline compounds which are generally found it in comparatively small quantities. In natural and fertile s these salts are already present, either in an active or soluble n, or else in the passive or insoluble condition, stored up in s which have not as yet become disintegrated by exposure to weather.

(1502) *Liebig's Classification of Crops by their Ashes.*—In er to ascertain the nature of the salts which are essential to the wth of any plant, Liebig insisted on the importance of an analysis he ashes obtained by burning such plants, grown upon a soil which nown to suit them; and in accordance with this suggestion, eat number of careful analyses of the ashes of the more imtant varieties of cultivated plants have been made both on continent and in this country. From the results thus obed it appears, *1. that the* number of the mineral constituents of plants is comparatively small; 2. that the nature of the mineral constituents varies in different tribes of plants; and 3. that it varies even in different parts of the same plant.

Potash, soda, lime, magnesia, with now and then small quantities of alumina, oxide of iron, and oxide of manganese, are the bases found in vegetable tissues; and they occur in combination with sulphuric, silicic, and phosphoric acids, as well as with hydrochloric, and with various organic acids; the carbonates of these bases, which are so frequently found in the ashes of plants, are derived from the compounds of the organic acids with the alkalies which the plant contains, and which are destroyed when it is burned.

Liebig has proposed to class vegetables for agricultural purposes according to the composition of their ashes, and the following Table will give an idea of the general principle which he has adopted. It will be observed that the same plant may appear in two different columns, as though it belonged to two different classes. The ash of the tubers of the potato, for example, is rich in alkaline salts, whilst the haulm abounds in salts of lime; hence, as is shown in the second subdivision of the Table, the potato should be regarded as belonging to the alkalino-calcareous class:—

Alkaline.	Calcareous.	Siliceous.
Maize (straw) Turnips (roots) Beet Potatoes (tubers) Jerusalem artichokes (tubers)	Tobacco Peas (straw) Potatoes (haulm) Clover Jer. artichokes Turnips (tops)	Wheat Barley Oats Rye } stem.
Alkalino-calcareous.	Calcareo-siliceous.	Alkalino-siliceous.
Peas Jerusalem artichokes Potatoes Turnips	Barley	Wheat Oats Rye

The results of such analyses suggest a probable reason why plants of different species do not all thrive equally well in a soil which may be highly productive for a particular crop; since a soil which abounds in the saline matters required by one crop may be deficient in the ingredients necessary for the full development of plants of a different species. Root crops, and succulent plants generally, require abundance of alkaline and calcareous salts; and experience has shown that the green shoots of all plants are those which contain these constituents in the largest proportion; the grasses, and plants with stiff but not woody stems, are rich in silica; while the grain crops, and seeds in general, as well as those plants which are richest in azotised nutritive materials, abound in the phosphates of the alkalies and of the earths.

Not only does the composition of the ash vary in different plants, but its quantity varies also within wide limits. According to the estimate of Johnston, a ton of each of the following substances in its undried condition, contains upon the average the under-mentioned proportions of ash:—

One ton of	lb. of ash.	One ton of	lb. of ash.
Potato tops contain .	26	Wheat straw contains	220
Turnip tops „ .	48	Oat straw „ .	140
Hay contains from	90—180	Barley straw „ .	110
Pea haulm contains .	100	Rye straw „ .	60
Bean straw „ .	70	Rape dust „ .	120

It is evident that all plants must, to a certain extent, deprive the soil of its *saline* components; since no plant adds anything to these materials which already exist in the soil, but on the contrary, every crop that is carried off removes with it a corresponding amount of mineral material. Owing, however, to this important and undeniable fact, to which public attention was first strongly directed by Liebig, many persons have been tempted to overlook the necessity of organic materials in the manure; and considerable disappointment has often been experienced in finding that the restoration of mineral matters to the soil was not the only condition required to renew, or to preserve its fertility. Messrs. Lawes and Gilbert have rendered essential service to agriculture by their admirable researches upon this point, which have recalled public attention to a circumstance of cardinal importance to the agriculturist.

(1503) *Modes of Action of Manures.*—It would be a serious mistake to suppose that a supply of the proper manure can always be predicated from a knowledge of the composition of the ashes of a plant, or from the analysis of the soil to be manured. Manures may act in one of three principal ways:—1. as direct food for the plant; 2. as what, for want of a better term, may be viewed as stimulants to its growth at a particular stage; and 3. as chemical agents which modify the constitution of other substances already present in the soil. Liebig has specially called attention to the first of these modes of the action of manures. The second of these methods has been particularly elucidated by Lawes, who showed that in the early stage of the growth of turnips, no manure is to be compared in efficacy with superphosphate of lime; although the plant itself contains so small a proportion of phosphates that it was precisely that plant fixed upon by Liebig, on theoretical grounds, as the one which from its non-requirement of phosphates was particularly well calculated to be grown upon land which might have been supposed to have been exhausted of its phosphates by a previous wheat-crop. It is now well known to the practical farmer, that the superphosphate when drilled in judiciously with the turnip seed, stimulates the growth of the plant in the earliest and most critical stage of its existence, and thus secures a far more abundant return than when the supply of superphosphate is omitted.*

The experiments of the same patient and indefatigable agriculturist, which have been carried on in conjunction with Dr. Gilbert, in a systematic manner, and upon a large scale for several consecutive years, have shown to the satisfaction of unprejudiced observers that the direct supply of phosphates to wheat crops frequently does not materially increase the produce, because ordinary wheat land already contains a far larger proportion of phosphates distributed through it than is necessary to the growth of many successive crops of wheat. This circumstance appears to be in great measure dependent upon a peculiarity in the mode of growth of the wheat plant; it strikes down the fibres of its roots to a great depth into the earth, by which means it is enabled to appropriate the phosphates of a much larger extent of soil than can come within the reach of the short tuft of fibres which constitutes the root of a crop like the turnip.† It is also found, and apparently for similar reasons, that the addition of silicate of potash as a manure does not materially strengthen the stem in wheat, but that the employment of ammoniacal manures, including the best varieties of guano, enables large crops of wheat to be raised for several consecutive years on the same piece of land, the ammonia appearing to supply nitrogen to the gluten of the wheat, and acting also as a general stimulant to the growth of the plant. But although this has been established as a scientific fact, it is not recommended that this practice be substituted for the system of rotation at present in use; though it appears that with the aid of nitrogenous manures wheat may be grown in larger quantities, and more frequently in the rotation, without injury to the fertility of the soil.

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* It is, however, probable that no manure acts simply as a stimulant, but that all such manures enter into the composition of the plant itself. These stimulating manures appear to supply through certain stages of the plant's growth a constituent or constituents, which, though present in the soil, may not be so in a sufficiently concentrated form, or which, owing to the imperfect development of the root, may not be sufficiently within the reach of the plant at the particular time when they are most needed.

† An interesting illustration of the influence of the development of the root upon the nature of the manure required, is afforded by a comparison of wheat and barley, which contain similar mineral constituents in nearly the same proportions:—wheat sown in autumn makes root all the winter, and is enabled to extract saline matters from the soil to a great depth; consequently it is seldom benefited by mineral manures directly applied, though it is greatly affected by the general mineral riches of the soil. Barley, on the other hand, is sown in spring; it throws out and depends upon root fibres nearer the surface, and is frequently much benefited by the use of manures containing phosphates.

It is a matter of experience that land which will not grow two remunerative crops of the same kind in succession (wheat for instance) without intermediate manuring, will yet, after a succession of turnips, barley, and clover, again be fit for wheat with comparatively light manuring; and that this system of rotation produces effects similar to those obtained by *fallowing*, or allowing the land to lie uncropped for a year. Lawes and Gilbert consider that clover and some other leguminous crops are especially valuable to the land, by supplying a quantity of nitrogenous organic matter to the soil, in a form particularly well calculated for assimilation by the succeeding wheat crop.

It is generally supposed that all the nitrogen found in combination in plants, has been obtained by the plant either from nitric acid or from ammonia, or from some azotised compound present in the soil in the form of manure; and that plants have not the power of directly assimilating nitrogen from the atmosphere. It appears tobe probable, however, that the leguminous plants generally introduced by the farmer in rotation, have a particular aptitude for condensing and retaining the nitrogen which is presented to them during their growth, and that they store it up; so that by the *débris* of their roots, and still more abundantly if ploughed into the land, they furnish a valuable source of nitrogen to succeeding crops. Wheat, on the contrary, accumulates but a comparatively small amount of nitrogen, and consequently thrives best when aided by the stimulus of manures containing that element. Lawes and Gilbert, however, found that the addition of 5 lb. of ammonia per acre in the form of manure, produced an increase of about a bushel of wheat; from which it would appear, calculating from the known composition of the corn and the straw, that not more than about two-fifths of the quantity of nitrogen supplied in the manure is retained in the gluten of the seed, in the straw, and in other parts of the plant.

Liebig accounts for the beneficial effects of the rotation of crops, by supposing that each plant in succession avails itself of saline matters which were unnecessary to the preceding crop. The process of fallowing appears to owe a certain portion of its efficacy to the gradual disintegration of the rocks, under the united influence of air, moisture, and alternations of temperature, in consequence of which, various substances, which were previously insoluble, are reduced to the soluble condition, and thus rendered available for the wants of the succeeding crop. It appears, however, to be probable, that the accumulation of compounds containing nitrogen within the soil during the period of fallow, has a material influence upon the following grain crop; but further experiments are still needed to elucidate the theory of fallowing.

The third mode in which manures act, viz., by the influence which they exert upon the components of the soil, is well exemplified in the application of lime, the most important uses of which are of an indirect character, although undoubtedly it is in some cases beneficial by supplying one of the mineral constituents essential to the healthy development of the plant.

Lime is applied to the land in the form either of slaked lime or of chalk. In the condition of slaked lime its chemical effects are exerted upon both the inorganic and the organic constituents of the soil. By its action upon the inorganic constituents, the insoluble silicates and the clays are decomposed: and potash, soda, alumina, and magnesia are set at liberty. Lime also decomposes salts of iron, rendering its oxide insoluble; it likewise partially decomposes common salt, forming carbonate of soda and chloride of calcium. The effects upon the organic constituents of the soil are even more important; for it is upon rich peaty soils which abound in organic matter, that the beneficial influence of lime is most evident. In such cases it occasions the decomposition of the organic matter, and gives rise to the formation of carbonic and nitric acids, as well as of ammonia; all of which bodies are important ingredients in the nutriment of the young plant; and at the same time the lime also liberates the saline constituents of a former vegetation, leaving them in a state well fitted for assimilation by the growing crop. This decay in the organic matter is produced by the simultaneous action of lime, atmospheric air, and moisture: it therefore takes place most rapidly near the surface, and is attended with the formation of nitric acid and ammonia, at the expense, in part, of the nitrogen of the atmosphere, just as occurs in the artificial nitre beds of Sweden, France, and other countries of the Continent. Similar effects are produced, though much more slowly, by the action of chalk or carbonate of lime; and the beneficial results occasioned by the application of chalk are consequently less immediately perceived, and are diffused over a longer period of time.

In connexion with this indirect action of manures, it may be mentioned, that the beneficial effects of carbonic acid on the growth of plants are not limited to its direct action in supplying carbon to the crop; it performs a function not less important, owing to its solvent power. The carbonates and phosphates of lime and of magnesia, and the oxide of iron are insoluble in pure water, but they are all dissolved to a small extent by water charged with carbonic acid, and are thus rendered available to the nutrition of the plant.

(1504) *Varieties of Manures.*—It has already been stated that the most important manures are those which are furnished by the excreta of animals; *guano* is one variety of this kind of manure; it consists of the decomposing excreta of sea-fowl which have fed upon fish; from its origin it abounds in phosphates and in ammoniacal salts; *farm-yard manure,* both solid and liquid, and night-soil and urine are also manures of a similar kind. Phosphates are abundantly supplied by *bone dust,* which also contains a considerable amount of gelatin. In burnt bones the gelatin is destroyed. The so-called *coprolites,* which consist principally of phosphate of lime, are probably *débris* of extinct animals, found in the tertiary beds of the Norfolk 'Crag,' and when reduced to powder and mixed with about half their weight of sulphuric acid, furnish one source of the manure which is known as *superphosphate of lime.* In this compound, the sulphuric acid liberates a portion of phosphoric acid, under the influence of which a portion of the bone earth is rendered soluble.

In the foregoing facts we see strikingly displayed the mutual dependence of the vegetable and of the animal creation. If the plant be necessary to supply organized food for the animal, the animal in his turn ministers in a manner not less important to the support of the plant. The animal, with every breath that he draws, sends forth carbonic acid into the atmosphere, and supplies carbon, which may ere long form an integral portion of the growing plant; the excreta which he rejects as useless and noisome are greedily absorbed by the rootlets of countless tribes of vegetables; and when life no longer animates his frame, the muscular, the gelatinous, and the nervous tissues, *during* putrefaction, are returned to the atmosphere in the form of water, carbonic acid, ammonia, and sulphuretted hydrogen; whilst the hard and compact bony portions of his body gradually moulder into dust. These various compounds supply, it may be, future crops of wheat, of turnips, or of potatoes, with their necessary carbon, ammonia, or phosphates; and the crops thus raised, in time, furnish sustenance to other generations of living beings: thus the very molecules of carbon, of nitrogen, or of hydrogen, which once formed part of the body of the beasts of the forest of former ages, may again become portions of living, breathing animals, or may at this moment constitute a portion of our own corporeal system.

The ashes of wood, of peat, and of coal are also valuable as manures, since they return to the soil the mineral ingredients which were removed from it by the vegetation of which they formed a part. Hence the burning of heath or of turf upon waste land commonly renders it more fertile; for it not only furnishes a considerable amount of mineral manure in an available form, but it also assists materially in disintegrating the felspathic constituents of the soil, which are much more readily acted upon by air and moisture after being thus exposed to a moderate ignition, than when present in their natural condition. It is in the same way that the burning of stiff clay, and subsequently distributing it upon the land, is sometimes beneficial.

Specific manures are in some cases required for particular crops upon certain soils. *Gypsum* or sulphate of lime is a highly important manure for leguminous crops, such as clover, in cases where lime or sulphates are deficient. *Nitrate of soda* in other cases forms a useful top-dressing to barley. *Common salt*, when applied judiciously to land where this ingredient is wanting, has been known to produce excellent results; and the importance of *liming* under various circumstances has been already alluded to.

For the further prosecution of this subject the reader is referred to works on agricultural chemistry, particularly to Liebig's *Agricultural Chemistry*, Johnston's *Lectures on Agricultural Chemistry*, and to the papers of Boussingault, in the *Annales de Chimie*, of Lawes and Gilbert, of Way, and of Voelcker, in the *Journal of the Royal Agricultural Society*.

§ II. Nutrition of Animals.

(1505) *Chemical Nature of the Food of Animals.*—The food of animals is considerably less simple than that of plants. Even plants have no power of directly assimilating any elementary bodies with the exception of oxygen, though few compounds are less complicated in their constitution than water, carbonic acid, and ammonia. Animals, on the other hand, appear to require substances which have been elaborated by the organism of plants, and thus brought nearer to their own more complicated structure.

The best instance of an aliment fully capable of supporting life and expressly elaborated for that purpose, is furnished in the case of milk. Upon this the infant or young animal lives for some time exclusively, thrives, and grows rapidly; and as Prout has remarked, it contains four distinct principles, which may be taken as the types of the four chief varieties of alimentary substances. These types are, 1. the *aqueous;* 2. the *albuminous* or azotised, represented by casein; 3. the *saccharine,* supplied by sugar of milk; and 4. the *oleaginous;* to these ought to be added, 5. the *saline,* which is equally essential. It might, therefore, be anticipated that a suitable diet should contain a certain proportion of each of these principles; for, although the body possesses the power of altering and assimilating food to an extent varying greatly with the circumstances under which it is placed, yet experience has amply demonstrated that no one of these principles can be wholly withheld from any animal of the higher orders for a lengthened period without producing fatal results. It has been shown, for example, when animals are fed exclusively upon sugar, upon gelatin, or upon albumen, that they die of starvation; although when these different materials are given in mixture, the animal lives and thrives. It has also been observed that those aliments which are admitted to be the most nutritious, and which are most largely used as articles of food, are those which contain all these principles in due proportion. A good example of this kind is afforded in bread made from wheaten flour: its starch and sugar represent the saccharine principle, its gluten furnishes the azotised or albuminous material; water it of course contains; and it also furnishes the phosphates and other salts of the alkalies and earths, including chloride of sodium. It likewise contains small quantities of fatty or oily matter, though the amount of this constituent is hardly adequate to the wants of the system: this deficiency is, however, supplied by the common habit of eating it with butter, milk, fat bacon, or some other oleaginous substance.

Animals, however, appear to possess to some extent the power of deoxidising saccharine matter and converting it into fat. The removal of a certain number of equivalents of carbonic acid, of water, and of oxygen, from fruit sugar would furnish the elements of the ordinary *forms of fat;* for example :—

$$20\,(\overbrace{C_{12}H_{12}O_{12}}^{\text{Sugar.}}) = 2\,(\overbrace{C_{114}H_{110}O_{12}}^{\text{Stearin.}}) + 6\,C_2O_4 + 10\,H_2O_2 + 43\,O_4.$$

An interesting illustration of the artificial conversion of sugar into a body belonging to the series of the fats, is afforded in the production of butyric acid by the fermentation of a solution of sugar under the influence of casein (1114); and a striking proof of the convertibility of sugar in the animal economy into a fatty substance, is afforded by the experiments of Gundelach and others upon the feeding of bees. In these experiments it was found that the insects, when supplied with pure sugar only, secreted wax in abundance; about 20lb. of sugar being consumed by the bees whilst they were producing 1lb. of wax.

The exact relative value of the saccharine and oleaginous principles of the food is not clearly understood, but one important difference between their functions is made evident, in the mode in which fat admits of being stored up in the economy in a form which allows of its being subsequently absorbed when needed: fat thus appears to serve as a sort of fly-wheel in the nutritive economy.

(1506) *Plastic and Respiratory Components of Food.*—The staminal principles or constituents of food may be further arranged as proposed by Liebig, according to the uses for which they are destined in the animal economy; and—since the great objects of the supply of food are two, viz., 1. the renewal of the tissues after they have become effete; and 2. the maintenance of animal heat,—the constituents of the food may be considered in their relation to these two great functions; in which case they would be regarded either as *plastic nutritive materials*, which consist exclusively of the albuminoid principles, or as *respiratory food*, including the saccharine and oleaginous principles of Prout. Liebig estimates that some of the more important materials used as food contain these two principal modifications in the following proportions, the respiratory materials being all calculated, for the convenience of comparison, in the quantities of starch to which they would be equivalent:—

	Plastic azotised matter.	Respiratory materials reckoned as starch.	
Veal contains	10	1	
Hare's flesh	10	2	
Beef	10	17	
Horse beans	10	22	
Peas	10	23	
Fat mutton	10	27 =	11·23 fat
Fat pork	10	30 =	12·5 fat
Cow's milk	10	30 =	8·8 fat 10·4 sugar

	Plastic azotised matter.	Respiratory materials reckoned as starch.
Woman's milk	10	40
Wheat flour	10	46
Oatmeal	10	50
Rye flour	10	57
Barley	10	57
Potatoes	10	86 to 115
Rice	10	123

Fat, sugar, starch, and alcohol must be regarded as articles which supply respiratory materials only; and when from external circumstances, such as exposure to cold, there is a greater demand upon the respiratory function, there is an instinctive craving for additional quantities of food which furnish those substances, by which the temperature of the body is maintained above that of the surrounding air: thus the Laplander and the Greenlander drink train-oil, and are more prone to excess in spirits than the dweller in a more temperate climate. Alcohol, it must be observed, is not simply a respiratory food: it acts as a powerful stimulant upon the nervous system, and hence its effects are complicated. It is generally noticed that persons who are fond of pastry and sweetmeats, and consume them largely, have but little inclination for wine and alcoholic drinks, since the demand for respiratory material is supplied by the saccharine and amylaceous aliment taken; whereas, those persons who indulge largely in animal food have a greater craving for fermented drinks, which no doubt operate partially in supplying the deficiency in respiratory materials that such food exhibits.

The azotised ingredients of the food likewise evolve heat in the act of oxidation; but since these materials constitute the more highly elaborated, and less abundant, yet indispensable components of the food of animals, such a mode of consuming them must be considered as extremely wasteful; whilst at the same time these bodies are less perfectly adapted than true respiratory food, for the maintenance of animal heat.

From the table above quoted it appears that in milk and in the different varieties of corn (which are the most perfect forms of nutritive matter), the proportion which the plastic bear to the respiratory materials, are, 1 of the former, to from 3 to 6 of the latter. The proportions of these components, however, vary considerably in the food of different classes of animals, and their organs of digestion are modified to meet these differences. Thus the carnivora live on the flesh and blood of other animals, which in chemical and physiological properties are identical with their own, and which after digestion in the stomach are reduced to a soluble condition; in this form they are absorbed, and enter into the composition of the animal. In the herbivora the organs of digestion are more complicated, since their food contains only small quantities of nitrogen. It is found that animals require more or less food, in proportion as the compounds which contain nitrogen are less or more abundant in it. The nitrogen occurs in the food principally in the form of compounds which have the same composition as the albumen and fibrin of animals. Vegetable albumen and fibrin are the principles which furnish plastic nutriment to the herbivora, and if they be withheld for any protracted period, starvation ensues. Hence it appears that one essential condition to the maintenance of animal life is the assimilation of certain materials, which are identical in constitution with the principal constituents of the blood. Animals do not possess the power of forming these principles, yet they produce a multitude of others from them by their decomposition; for example, plants cannot produce the gelatinous principles, neither do they furnish the constituents of the brain, both of which are elaborated in the animal frame from the components of the food. The azotised compounds, when taken alone, are insufficient to support life; saccharine and oleaginous matters are absolutely necessary, and in the young, even of carnivora, they form, in the shape of milk, a most important part of their nutriment. Even the flesh diet of the carnivora contains a large proportion of fat, which supplies the necessary respiratory material.

In our estimate of the importance of the different materials which enter into the composition of food, we must not overlook the various salts; particularly common salt, phosphate of lime, and the sulphates and phosphates of the alkalies. Common salt is essential for the supply of the hydrochloric acid of the gastric juice, and the soda of the bile. Phosphate of lime is necessary to the building up of the bones; and not a cell or a fibre of the body can be formed without the presence of the soluble phosphates.

Liebig has pointed out the singular manner in which these different salts are associated in the different parts of the body; chloride of sodium, for instance, abounds in liquids which, like the blood and the serous exudations, have an alkaline reaction, and is commonly accompanied by tribasic phosphate of soda. Phosphate of potash, on the other hand, occurs in liquids which, like the juice of the flesh, have an acid reaction.

(1507) *Process of Digestion.*—The preliminary cooking to which much of our food is submitted, is not essential to the process of digestion, but is generally resorted to in order to please the palate; but where a mixture of many kinds of food is to be assimilated by the stomach, the process of cooking may be made to assist the operations of digestion. The principal steps by which the food, after its reception into the mouth, is converted into a part of the living organism, are the following:—The food is first masticated and thoroughly mixed with the saliva. Animals which are carnivorous, chew their food less completely, and are supplied less abundantly with saliva, than those that are herbivorous. The reason is obvious, since in the carnivora, the fleshy nature of their aliments enables the latter to be more readily assimilated than is the case in the herbivora, many of which, by ruminating, subject their food a second time to a thorough trituration and intermixture with the saliva. Birds that are granivorous, are furnished with a strong hollow muscle, the gizzard, which is especially designed for the purpose of triturating the seed, to aid which, the birds swallow pebbles and gravel. The food, having been masticated and reduced to a pulp by intermixture with the saliva, is next transferred to the stomach, where it becomes mingled with the acid secretion of the gastric juice (1481). After remaining for a few hours in this organ, the principal proportion of the albuminous and fibrinous constituents of the food is brought into the liquid form; but the fatty matters remain unaffected, and the starchy components are but imperfectly converted into the soluble form of dextrin, or of sugar. From the stomach, the food, now reduced to a pultaceous mass termed *chyme*, passes to the duodenum, or commencement of the intestinal canal, where it is mixed, first with the secretion from the liver, and then with that from the pancreas.

Physiologists are not agreed upon the share which the bile takes in the function of digestion, but both the bile and the pancreatic secretion are alkaline, and the chyme immediately after admixture with these liquids, assumes the appearance of an emulsion; in its further passage along the intestinal canal, it is mixed with a secretion from the inner surface of the jejunum and of the ileum, which still further modifies the food, completing the conversion of starch into a soluble compound, and rendering the fatty matters capable of assimilation. In the small intestines a separation of the aliment into two portions is effected; the larger of these portions is absorbed into the system, the smaller portion, consisting of vegetable fibre and insoluble and undigested matters, becomes excrementitious, acquiring a peculiar odour, and is ultimately rejected. The absorbed portion is taken up partially as a thin, milky liquid (the chyle), which is absorbed from the inner surface of the intestines by the lacteals, and these vessels empty themselves through the thoracic duct, into the subclavian vein: a still larger portion is absorbed by the mesenteric veins, which transmit their contents to the liver, to be there further elaborated before they are transferred by the hepatic veins to the right auricle of the heart.

One principal change wrought in the food, during its conversion into chyme, consists in its being rendered soluble, and combined with water; but it is evident that the mere fact of the conversion of the food into the liquid form, is by no means the only essential condition, since soluble matters, such as the casein of milk, are frequently first converted into a solid form in the stomach, and are then gradually redissolved; the elements of the food are thus rearranged, and if casein be the substance acted on, it is converted into albumen; but the principal change is that described by Prout as the *vitalizing* action of the stomach,—that change which fits dead organized matter for again becoming a portion of the living frame. The nature of this change is not at all understood. The solid form in which azotised matters are generally presented to the stomach, may be designed (by demanding a longer stay in this organ) to facilitate and allow time for the completion of this change; whilst the amylaceous and oleaginous principles of the food, which simply supply the respiratory fuel, do not require so long a stay in the stomach. It is worthy of remark that albumen, even after it has been given as the sole constituent of the food, when it has once been dissolved, cannot be detected as such in the fluid of the stomach, either by boiling or by the action of nitric acid; it is not till after it has passed through the duodenum, and becomes mixed with the secretions of the liver and the pancreas, that albumen manifests itself by the ordinary reagents.

When digestion is duly performed, no gaseous products are set free; but when it is faulty, we often have a train of symptoms more or less distressing, owing to the evolution of carbonic acid, nitrogen, and hydrogen gases, which produce painful flatulence and distension. It may be to render this distension less liable to occur in infants, that milk contains an unfermentable variety of sugar.

There is a very great difference in the digestibility of the different articles used as food; some being completely chymified in two hours, and others requiring as much as six before this effect is produced. Very slight circumstances frequently interfere with the digestive process. Fats are apt to disagree, and so are all substances into the composition of which they enter largely; such as pastry, rich stews, and fried dishes; owing partly to the production of the peculiar volatile acids of fat during the processes of cooking or digestion, and partly owing to the difficulty with which such food is penetrated by the gastric juice. Where such food has been taken, the assimilating powers of the stomach are often interfered with, and the injurious effects thus occasioned are frequently manifested in the form of a sick-headache. Fermented liquors, if taken in small quantity, often afford a healthy stimulus to the stomach, but if taken in excess they arrest digestion and produce serious disturbance, independently of their enervating effects.

(1508) *Nutrition and Disintegration.*—Having traced the food into the blood, by the process termed by Prout *primary formative assimilation*, we may pass on to consider the course by which it becomes incorporated with the tissues of the living body. The offices of the blood may be considered under three principal heads:—1. that of *nutrition*, or reparation of the effete parts of the corporeal frame; 2. that of *respiration*, or the maintenance of animal heat; and 3. that of *secretion*.

1. *Nutrition.*—There is abundant evidence to show that the various tissues of the body are undergoing a constant succession of changes which are essential to the maintenance of life, and that the more actively the vital powers are exerted, the more rapidly do these various changes occur, necessitating the supply of food more frequently and abundantly. Shortly after the deposition of any particle has taken place in any particular tissue, it is in its turn removed to make room for a new and equally fleeting successor. This deposition of new matter is termed by Prout *secondary formative assimilation*, in opposition to the *secondary destructive assimilation*, by which the removal of the effete particles is effected. The principal organs of the body consist of albuminous and muscular tissue, with the exception of its solid framework, and of those peculiar compounds which constitute the mass of the brain and of the nerves. Albumen and fibrin, the basis of these tissues, are contained ready formed in the blood, and they appear to be deposited at those points where they are needed, by a process somewhat analogous to that of simple coagulation. No advantage, however, would be gained, if the portions which they displace were to be re-absorbed in the form of albumen or of fibrin into the mass of the blood; for the deposited particles having once discharged their function in the system, cannot again be admitted to form integrant parts of it, until, as in the case of the

albuminous and fibrinous portions of animals taken as food, they have been again subjected to the process of digestion, and have thus been fitted by the stomach for the performance of their various functions. The change which attends the absorption of matter once deposited is deep-seated, and is essentially connected with the manifestations of vital activity. No portion of albumen or of fibrin seems to be removed, as such, into the system; consequently the fibrin and albumen contained in the blood in a healthy state, must be considered as freshly elaborated, and as existing in it as a preliminary to its constituting an integral part of the body; and, therefore, as being in a form ready for assimilation. The effete tissues are decomposed at the moment of their removal, and are converted by the process of absorption into new and distinct compounds; thus furnishing the second source whence the blood derives its component parts, the process of absorption constituting the *secondary destructive assimilation* of Prout. This removal is usually effected by the agency of oxygen, supplied during respiration, and carried by the blood to every part of the system: the organic particles thus removed are therefore in a more oxidized form than that in which they were deposited, and they are absorbed at first into the blood itself, from which they are quickly eliminated in some of the excretions from it. Thus the nitrogen is removed partly in the form of urea, or of uric acid, and partly in that of ammonia. The carbon is chiefly got rid of as carbonic acid; and the phosphorus and sulphur, as phosphoric and sulphuric acids. These different matters are eliminated through four principal sources, viz. 1. the excreta of the alimentary canal; 2. the urine; 3. the cutaneous excretions; and 4. the pulmonary exhalation. Having already considered the principal chemical relations of the first three excrementitious products, we shall now confine our attention to the nature of the pulmonary exhalation.

(1509) 2. *Respiration.*—The important function discharged by the lungs consists in the admission of atmospheric air into the body, in such a manner as shall enable it to act upon and oxidize the blood; the most obvious chemical change which is produced in the respired air, consisting in the abstraction of oxygen from it, and the substitution of a bulk of carbonic acid nearly equal to that of the oxygen removed. The lungs act as an immense filter through which, in the higher classes of animals, the whole mass of the blood is made to circulate as often as it passes through the heart. The venous blood as it arrives in the lungs is of a deep purple colour. It leaves them of a florid arterial red. The general structure of the lungs is such that these organs may be regarded as consisting of two sets of tubes, the larger of which is for the admission of air. The air-tubes are subdivided into an infinite number of small ramifications, around which the blood-vessels are distributed in an extremely fine network; by this arrangement an immense surface is exposed to the air, with a comparatively small expenditure of space. The lining membrane of the air-tubes is kept continually moist by the secretion from their surface. Through this delicate membrane air passes readily by endosmosis into the blood-vessels beneath, and in consequence of this action the venous blood exchanges a portion of its carbonic acid with the oxygen held in solution by the liquid which bathes the surface of the air-tubes. The oxygen in this form obtains admission into the current of the circulation.* The mere displacement of carbonic acid from the blood, although unattended with any perceptible chemical change, produces an alteration of colour from purple to scarlet. During the circulation of the aërated blood through the minute capillary vessels of the body, the absorbed oxygen effects those chemical changes which are essential to the maintenance of animal life. The tissues are broken up; urea, carbonic, lactic, uric, sulphuric, phosphoric, and perhaps other acids are formed; these are removed by the kidneys, the skin, and the lungs. Whilst these decompositions are being effected, fresh particles, of constitution similar to the tissues undergoing decomposition, are being deposited from the blood, which receives the acid products, and is thus materially altered in colour and constitution. When the blood again passes through the lungs, the carbonic acid is mechanically displaced from it by oxygen, and the scarlet colour is restored, whilst the other principles are in great part eliminated by the kidneys.

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* During the process of respiration a small quantity of nitrogen as well as of oxygen is absorbed, and this probably is one source of the nitrogen which is undoubtedly exhaled by the skin. It is probable that this nitrogen undergoes no chemical change, but is merely mechanically taken into the system owing to its solubility; the quantity in the air does not appear materially to vary, because if the blood be saturated with nitrogen, the amount of this gas which is separated will be equal to that which is evolved. By making animals respire in an atmosphere of oxygen and hydrogen, nitrogen is always found to be given out, since it is displaced from the blood by the hydrogen. According to the experiments of Regnault and Reiset (*Ann. de Chimie*, III. xxvi. 511), warm-blooded animals, if made to respire in a confined space, always exhale an appreciable quantity of nitrogen; the amount, however, of this is so small, as not to exceed $\frac{1}{100}$th part of the quantity of oxygen consumed. When the animals were in a state of exhaustion from want of food, an absorption of nitrogen commonly occurred to a similar extent. Traces of hydrogen, of carburetted hydrogen, and of ammonia are also present in respired air.

It is probable, from the experiments of Magnus, that a portion at least of the oxygen absorbed by the arterial blood, is not actually in a state of chemical combination with it. Water is not capable of dissolving more than about one-fortieth of its bulk of oxygen, and the solvent power of serum is not materially different. Consequently, each pound of blood could not dissolve more than about three-fourths of a cubic inch of oxygen; but direct experiments have proved (supposing 10lb. of blood to pass through the lungs per minute) that the average quantity of oxygen absorbed is not less than three times that amount. Hence it is difficult to account for the absorption of so large an amount of oxygen, without admitting a species of combination with the components of the blood; although this combination must be of such a nature that the oxygen is readily imparted to the components of the body when the blood reaches the capillaries.

The red particles appear to be intimately concerned in the process of conveying the oxygen; but the precise mode of their operation is unknown. There seems, however, to be but little doubt that the greater part of the chemical change is effected by the oxygen after it reaches the capillary vessels which constitute the great laboratory of the body, for until it reaches these minute branches, the blood retains its florid hue, but on its exit from them it has the dark tint of venous blood.

(1510) *Proportion of Carbonic Acid exhaled during Respiration.*—The earliest trustworthy observations upon the chemical changes produced during respiration are due to Lavoisier and to Seguin, and since their time numerous eminent chemists have made this process an object of study; particularly in relation to the quantity of oxygen consumed, and of carbonic acid produced. Much discrepancy, however, existed among the earlier statements regarding the quantity of carbonic acid contained in the respired air. We are indebted to Prout for a satisfactory explanation of these differences, which he proved to arise mainly from the fact that the quantity of carbonic acid varies in the same individuals at different times; and the numerous careful experiments published subsequently to those of Prout have fully established the correctness of these observations. It appears that the proportion of carbonic acid exhaled in a given time by the same animal, varies according to the rapidity of the circulation: the more vigorous the circulation, the larger is the quantity of carbonic acid evolved: thus, *cæteris paribus*, a larger quantity is formed after a meal than when the animal is fasting; the proportion is also higher when the animal is awake than when sleeping.

An important series of direct experiments upon respiration in man was undertaken by Scharling (*Liebig's Annal.*, xlv. 214, and lvii. 1). Other experiments upon the same subject by Andral and Gavarret will be found in the *Annales de Chimie,* III. viii. 129. Still more recently, Regnault and Reiset have published an extensive and elaborate series of researches upon the respiration of various classes of animals, from which several new and important conclusions have been deduced (*Ann. de Chimie,* III. xxvi.)

Scharling's experiments were performed upon persons of different ages who were placed in an air-tight chest, freely supplied with atmospheric air, which was deprived of carbonic acid by causing it to pass through a solution of potash. The respired air was transmitted through a succession of vessels, filled with sulphuric acid in order to retain moisture, with solution of potash to retain carbonic acid, and with sulphuric acid to retain moisture which the current of air might mechanically carry over from the solution of potash. The increase in weight of the last two vessels indicated the amount of carbonic acid. A continuous current of air through the apparatus was maintained by means of the regulated action of an air-pump, and the quantity of carbonic acid contained in the air of the chest at the close of the experiment was determined by direct analysis. By means of experiments conducted with this apparatus, it was ascertained that, on an average, the production of carbonic acid during sleep amounted only to three-fourths of that given out by the same individual for an equal interval of time during the period that he was awake. It was also found that the production of carbonic acid was proportionately greater in children than in adults, as was to have been anticipated from the greater activity of the vital functions during the period of growth and development. The average production of carbonic acid was also greater in male than in female adults, as might be expected from the smaller size of the latter: but in adult individuals of both sexes, if of equal weight, *cæteris paribus,* the consumption of carbon appeared to be nearly equal. The same observer has also shown that the quantity of carbon exhaled in the form of carbonic acid from the surface of the skin, in the adult, does not on the average exceed one-third of an ounce in the twenty-four hours. In cold-blooded animals, however, the respiration effected through the skin is much more extensive; frogs and salamanders will continue to live for several days after the lungs have been removed, owing to this cutaneous respiration (Regnault).

The average quantity of carbon which passes off during the day from the lungs and skin of an adult man is estimated by Dumas at about 8½ ounces avoirdupois. These results have been almost exactly confirmed by the more recent experiments of Scharling. Andral and Gavarret found in their experiments that the quantity of expired carbonic acid was nearly the same as that given by Scharling. Liebig's estimate is considerably higher; but it is probably less correct, since it was not founded on direct experiment, but was inferred from a rather loose estimation of the average amount of carbon contained in the rations allowed to a regiment of soldiers; making a somewhat arbitrary deduction for the amount of carbon eliminated in the urine and fæces.

It is, however, obvious that the amount of carbonic acid, and the proportion which it bears to the respired oxygen, must vary with the nature of the food. When carbon is converted into carbonic acid, the volume of this gas which is formed is exactly equal (under similar circumstances of temperature and pressure) to that of the oxygen which has entered into its composition; but when hydrogen is oxidized, the whole of the oxygen with which it has combined disappears from the gases exhaled; and a similar remark applies to that portion of oxygen which enters into combination, so as to form solid or liquid azotised compounds. It can therefore only happen that the proportion of carbonic acid expired and of oxygen consumed shall be equal, when the whole of the inspired oxygen is employed in the oxidation of carbon. The direct experiments of Regnault and Reiset have, however, shown that this variation in the proportions of carbonic acid, and of respired oxygen, lies within very wide limits. From similar causes, when much fat is taken with the food, a large portion of oxygen disappears. Thus it may be proved by calculation that when butter supplies the respiratory food, for every 31 volumes of oxygen absorbed, 21 only of carbonic acid can be produced; and a similar, but smaller, disappearance of oxygen occurs when alcoholic liquors have formed part of the food consumed. Regnault and Reiset found in their experiments, that dogs, when fed on meat, exhaled about 74 volumes of carbonic acid for 100 volumes of oxygen absorbed; but when fed on amylaceous substances the quantity of carbonic acid rose to 93 per cent. A dog which had been fed upon mutton suet, emitted only 69·4 per cent. of carbonic acid; the deficiency being in this case consumed in converting the excess of hydrogen in the fat into water. When animals which had been long kept without food were subjected to experiment, the percentage of carbonic acid was about the same as when they were confined to an animal diet; because the tissues of the animal constituted the source whence the carbonic acid was supplied; the animal was, in fact, feeding upon its own flesh. Rabbits fed upon vegetables emitted from 85 to 95 per cent. of carbonic acid, compared with the volume of oxygen absorbed; and granivorous birds yielded from 90 to 103 per cent., the volume of carbonic acid frequently exceeding that of the oxygen consumed. When these birds were confined to a flesh diet, the quantity of carbonic acid fell to about 67 per cent. of the oxygen consumed.

In the course of these experiments it was ascertained that, provided the quantity of oxygen be proportionately increased, an animal may continue to breathe without injury in an atmosphere containing a considerable amount of carbonic acid; the injurious effects of carbonic acid in the air appearing to depend rather upon the mechanical obstacle which it offers to the escape of the gas already in the blood, than to any directly poisonous action of the carbonic acid itself. By increasing the facility for its diffusion by the addition of oxygen, or even of hydrogen, to air already containing a considerable quantity of carbonic acid, the animals may continue to breathe such air without injury. Regnault found that the proportion borne by the carbonic acid exhaled, to that of oxygen consumed, is not altered when pure oxygen is substituted for atmospheric air, and the same relations were observed when the animals were caused to respire in an atmosphere consisting of a mixture of oxygen and hydrogen.

An interesting illustration of the great differences in the mode of respiration which may occur even in the same animal under altered circumstances, is afforded by the observations upon hybernating animals. Marmots were found during their torpid condition to consume not more than one-thirtieth of the amount of oxygen which they required in their active state. These animals at the commencement of their hybernation are fat, but they lose weight considerably before they resume their active condition. A remarkable observation upon these animals was made by Sacc, and confirmed by Regnault and Reiset. The marmot whilst in a torpid condition increases in weight, owing to an absorption of oxygen which amounts to nearly one-half of that inhaled; this oxygen becomes converted into water, the greater portion of which is retained in the system for a while, but the animal at intervals evacuates it from the bladder, so that in the long run its weight becomes diminished. In fact, during its sleep its temperature is really maintained by the slow combustion of the store of fat which it had accumulated previous to its winter's repose.

The air which has passed through the lungs in the ordinary process of respiration, is by no means deprived of its oxygen; it usually contains about 4 per cent. only of carbonic acid; the greater portion of the air which is expelled during expiration has not proceeded further than the larger ramifications of the bronchi. In ordinary respiration 30 cubic inches, or about one-fifth, of the quantity of the air in the lungs is changed with each act of respiration. The number of respirations in a healthy adult averages per minute from 18 to 20, but the bulk, as well as the frequency, of the inspiration varies with each individual, according to the circumstances in which he is placed, and the necessity of a larger or smaller supply of oxygen to the system. Assuming that the volume of air respired each time is 30 cubic inches, and that 20 respirations occur per minute, not less than 500 cubic feet of air would pass through the lungs of each individual in 24 hours.

If we assume that the average evolution of carbon by the lungs of an adult man amounts to 8·5 ounces avoirdupois in twenty-four hours, it is easy to calculate the quantity of oxygen which is required during respiration for that period:—8·5 oz. of carbon would require about 22·66 oz., or 16·73 cubic feet of oxygen for its conversion into carbonic acid, and would yield 28,912 cub. in. of this gas at 60° F., barometer at 30 inches,—or 21 cubic inches per minute: consequently, if 10lb. of blood pass through the lungs per minute, every pound of blood, in its passage through these organs must emit about 2 cubic inches of carbonic acid. Now, since for the oxidation of 8½ oz. of carbon, 22·66 oz. of oxygen are required, and since it is found that an adult emits on the average a volume of carbonic acid equal to 85 per cent. of the oxygen inhaled, it may be inferred (allowing 15 per cent. for the amount of oxygen fixed by hydrogen, &c.), that not less than 26·7 oz., or upwards of 1½lb. of oxygen, are daily consumed by every adult; and allowing for 1·4 oz. of dry solid matter evacuated by the intestinal canal, and 2·2 oz. of solids by the urine, the whole of the remaining portion of the food (exclusive of about 4½lb. of water, which is eliminated by the kidneys and the skin), must pass off in the gaseous form by the lungs.*

The exact form in which the compounds which are destined to produce animal heat exist in the blood is unknown, but there can be no doubt that the permanently alkaline condition of the blood (which Liebig attributes to tribasic phosphate of soda in the carnivora, and Lehmann to carbonate of soda in the herbivora) is concerned in a very important manner in this oxidating process: for it is uniformly observed that compounds of organic origin are much more readily oxidized in the presence of alkalies than they are when in a neutral or in an acid condition; doubtless because the products of oxidation being commonly acid, the presence of a base with which those acids can combine facilitates the formation of the acid, whether it be carbonic or any other acid compound.

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* The results obtained by Barral upon the average assimilation and con-

(1511) *Animal Heat.*—The temperature of the human body, whatever may be the temperature of the atmosphere, is uniformly maintained at 98° or 100°, that of birds at from 106° to 108°,

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sumption of food in twenty-four hours during summer and winter, conducted upon his own person, may here be cited (*Annales de Chimie*, III. xxv. 129).

Quantities in oz. avoirdupois of Food and Excreta in twenty-four hours.

Period of the Year.	Consumed.			Evolved.				
	Food taken.		Oxygen absorbed.	Water by skin and lungs.	Carbonic acid.	Total excreta.		
	Solid not dried.	Liquid.				Urine.	Fæces.	Nasal secretions.
						Not dried.		
In July . . .	24·4	59·7	27·42	40·27	31·34	36·14	2·66	1·19
In December .	39·2	57·9	37·44	45·43	43·32	39·97	5·00	1·15
Or in 100 parts.								
In July . . .	75·4		24·6	36·1	28·8	34·7		0·4
In December .	72·2		27·8	33·8	32·3	33·2		0·7

Although these results are not free from objection, they possess considerable interest. The amounts of carbonic acid emitted and of oxygen absorbed are inferred from the difference between the quantity of carbon, hydrogen, and nitrogen found by analysis in the food taken, and that furnished by the solid and liquid excretions. This mode of calculation necessarily involves these numbers in some uncertainty, since all the errors of experiment fall upon them. It was found that the total quantity of oxygen absorbed amounted to fully one-third of the entire weight of the solid and liquid constituents of the food. The proportion of nitrogen to that of carbon contained in the food taken was as 1 : 12·8. The excess of nitrogen in the food over that of the solid and liquid excretions varied from one-third to one-half; and this excess must have passed off through the skin and lungs; but this estimate is probably too high, although it does not attain to much more than 1 per cent. upon the volume of the carbonic acid. The proportion of nitrogen found in the solid excreta did not amount to one-fifth of that contained in the urine.

The proportion of carbonic acid exhaled in winter is much greater than in summer, and the quantity of water is also a little greater in winter. The latter circumstance may be explained by the fact, that more air passes through the lungs in winter than in summer, and it is less loaded with moisture on entering them; but in both cases the air quits them saturated with aqueous vapour at the temperature of the body, consequently it will carry off more moisture in the winter than in summer.

and that of warm-blooded reptiles at about 85°. But as the temperature of the air is many degrees, in this climate often 40° or more, below that of the human body, it is clear, since the animal frame is subject to cooling at the same rate as other natural objects, that a constant supply of heat is necessary to the maintenance of this steady temperature. In order to diminish the quantity of heat required to be generated, animals are furnished with coats of hair, of feathers, of wool, and of other light, porous, non-conducting materials, which greatly retard their rate of cooling, and the thickness of which varies with the season of the year, and the average temperature to which the animal is exposed. Man supplies himself with clothing, which experience teaches him to adapt to the varying circumstances under which he is placed.

This constant evolution of heat in the living body is occasioned by the gradual combustion of the carbon and of the hydrogen supplied in the food; the combustion being effected by the agency of the respired oxygen. All bodies, when they enter into combination with others, whether quickly or slowly, evolve heat, and when the products resulting from combination are the same, the amount of heat which is developed for the same weight of the compound produced is also identical (1527). Carbon and hydrogen are already combined with each other in the body, and in the act of their combination have already evolved a certain amount of heat; the combustion of a hydrocarbon, therefore, will not produce the same amount of heat, as the combustion of an equal quantity of carbon and hydrogen not previously in a state of combination; still a very large quantity of heat will be developed during their oxidation, and if this oxidation be effected within the body, the heat thus liberated will necessarily contribute towards maintaining the temperature of the body. According to the experiments of Despretz, 1 ounce of pure carbon during combustion evolves heat enough to raise the temperature of 14,200 times its weight of water through 1° of F., or enough heat to convert into vapour 12·63 times its weight of water at 100°, or the temperature of the body; the heat developed by the combustion of 8·5 ounces of carbon should, therefore, suffice to evaporate 107·7 ounces of water daily, or nearly 6·75lb. This quantity of water is more than double the average amount of that which is actually exhaled from the entire body in the twenty-four hours, the average being about 1 lb. from the lungs and 1½ lb. from the skin. The surplus heat from the carbon, as well as that from the hydrogen, the amount of which is not so easily estimated, is expended in keeping up the temperature of the body. Experiments have shown that animals exhale more carbonic acid in proportion to their weight, as their temperature is higher. It has been estimated that birds evolve half as much carbonic acid again as the mammalia do; but Regnault finds that, in some cases, the disproportion is much more considerable. The smaller the animal, the larger is the proportionate extent of its cooling surface, and consequently the larger is the quantity of carbon which must be oxidized within it in order to maintain a temperature equal to that of the larger animal; linnets, for instance, evolve 10 times as much carbonic acid in proportion to their weight, as the domestic fowl. Small animals consequently consume a much larger quantity of food in proportion to their weight than large animals, and this may account for the greater proportionate activity of many small animals when compared with larger ones.

Since the diffusion of animal heat over different parts of the body is tolerably uniform, the source of heat should be diffused likewise. Provision appears to have been made for this essential condition, in the circumstance that the principal action of oxygen upon the constituents of the body takes place in the capillary vessels which are distributed throughout the whole organized structure; and therefore the heat resulting from this action is also equally distributed through the different parts of the body. A certain amount of chemical action doubtless takes place in the lungs, where the blood first comes into contact with the air, and this increased chemical action would be needed to supply the heat carried off by the vapour which passes off at each expiration; but the main oxidizing actions occur deep in the structures of the body itself.

(1512) *Demand for Food varies with the Temperature.*—Since, then, the combustion of the hydrocarbonous portions of the blood are required for the due production of animal heat, it might be expected that, as the demand for heat varies at different seasons and in different climates, the quantity and the quality of the food demanded should also vary accordingly. Experience proves that such is the case; the appetite is keener in winter than in summer, and the aliments which we are then in the habit of consuming partake more of a fatty and carbonaceous character: the inhabitants of the polar regions maintain the necessary supply of heat by an abundant consumption of blubber and train-oil,* while those who live in tropical climates content themselves with a lighter and more succulent vegetable diet. It is remarked by Liebig that the habits of life formed by the European are in some degree retained when he makes his abode under the burning sun of an Indian sky. Under such altered circumstances he still stimulates his appetite to consume the flesh diet to which he has been accustomed, and diseases of the liver are the consequence. This gland secretes a fluid rich in carbon, and in certain cases may act as one outlet of hydrocarbonous matters to the system. Respiration in a hot climate takes place with diminished frequency. It must also be remembered, that equal volumes of air admitted to the lungs by respiration at high and at low temperatures contain very different weights of oxygen; air at 40° containing one-tenth more by weight of oxygen than an equal bulk of air at 90°. Less carbon, therefore, is thrown off by the lungs in equal intervals of time, in a hot climate than in a cold one, by which means the too rapid production of animal heat is avoided; but the excess of carbon carried into the system must, nevertheless, be got rid of, and this must be effected in a manner that shall not produce heat. Owing to the beautiful compensating system upon which our bodies are constructed, one organ, if necessary, can relieve another from its burden, and the liver carries off this excess of carbon in an unburned form; provided the quantity be only moderate, this vicarious action may be effected without inconvenience, but if it be excessive, enlargement and congestion of the gland ensue, and disease, more or less serious, is the result. In a dry state of the atmosphere, however, less duty falls upon the liver, inasmuch as free evaporation goes on from the surface both of the lungs and of the skin, and thus the temperature of the body is reduced. In dry weather, therefore, carbon may be emitted by the lungs in larger quantity without inconvenience; but when the temperature of the air is high, and at the same time loaded with moisture, this source of relief is cut off, and an oppressive sensation of languor is experienced.

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* It is, however, difficult to say whence the whale and the seal in their icy climate derive the means of accumulating their stores of blubber and oil.

There is still a great want of accurate direct experiments on the production of carbonic acid under great differences of temperature, and a correct series of experiments on this subject, in arctic and in tropical regions, would be highly valuable both to the physician and the physiologist.*

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* Upon this point the experiments of Lehmann (*Lehrbuch der Physiologischen Chemie*, vol. iii. page 304,) may be cited. He found that 1000 grammes weight of pigeons yielded in *dry* air 6·055 grammes of carbonic acid per hour at 75°, and 4·69 grammes at 100°; the same animals in *moist* air yielded 6·769 grammes at 73°, and 7·76 grammes at 100°. And 1000 grammes weight of rabbits exhaled in *dry* air 0·451 grammes of carbonic acid per hour at 160°, and as much as 0·677 grammes in a *moist* atmosphere at the same temperature. Dr. E. Smith is also pursuing a laborious series of researches upon the exhalation of carbonic acid under varied circumstances.

On the whole, then, it appears that the saccharine and oleaginous portions of our food are those which are best adapted to the maintenance of respiration and of animal heat: when, however, these materials are given in excess, they are thrown off by the liver and the kidneys: Tiedemann and Gmelin found, when they fed animals on butter and starch, that the urine was loaded with fatty matter, and bilious diarrhœa was an almost constant attendant. The azotised principles of the food are necessary for the reproduction of the muscular and other tissues, and go to form the azotised principles of the blood; and hence the importance of a mixed diet for the due support of the vital functions. The nutritive value of different articles of food is, therefore, entirely relative, and is dependent upon the proportion in which each is mingled with other bodies, in which the four staminal principles are combined together in due proportion.

It must not be overlooked, however, that the most advantageous mixture of nutritive materials will vary with the circumstances under which the animal is placed. In the human species, the milk is adapted to the wants of the new-born infant, which will be wrapped in clothes, and shielded from the weather; and the materials consist of about 10 parts of plastic matter, 10 of fat, 20 of sugar, and 0·6 of salts. In the case of the cow, where the young animal is more exposed to the vicissitudes of the weather, the proportion of these constituents is altered, the milk containing to every 10 parts of plastic material, 11·11 of fat, and 14 of sugar. The composition of the milk at different periods of lactation also varies in an important manner, in order to meet the altering wants of the young animal in the successive stages of its growth.

A few animals are entirely carnivorous; but it must be remembered that all flesh, even that which is usually considered to be lean, contains, in addition to azotised matter, a certain quantity of the oleaginous or fatty principle which is needed for the support of respiration. The herbivora consume with their food large quantities of saccharine and amylaceous compounds, which, by the abstraction of oxygen, are converted into fat; such animals are capable of being fattened in a remarkable manner, whereas the carnivora seldom acquire any great store of fat, in consequence of a deficient supply of the material best adapted for conversion into that substance.

It has been already remarked, that when increased demands are made upon the strength of animals, as in taking exercise, the number of respirations is increased, and the circulation quickened, more oxygen is absorbed, and more carbonic acid evolved; and it appears to be probable that this increased demand upon the muscular effort is, for the time, supported by the increased stimulus resulting from the more rapid chemical action upon the tissues of the body. For a fuller consideration of the subject of animal heat, the reader is referred to Liebig's treatise on *Chemistry in its Application to Physiology and Pathology*.

(1513) 3. *Secretion.*—Having now considered the functions of the blood in regard to nutrition, and to respiration, we have lastly to offer a few remarks upon the process of secretion. It is worthy of remark that in every instance where a purely excrementitial product is formed, the substances excreted are produced in the mass of the blood, at a distance from the point at which they are separated. The bile furnishes an exception, but, as it has been already stated, the greater portion of this fluid is re-absorbed into the system; it therefore cannot be considered as purely excrementitious. In experiments in which the kidneys have been removed from animals, uric, phosphoric, and sulphuric acids, as well as urea, are found to accumulate in the blood; the kidney is, therefore, not to be looked upon as an oxidizing or acidifying organ, but as an organ through the agency of which acids are separated from the system, combined with, and nearly neutralized by, alkaline matters. A similar principle holds good in the case of the lungs, which may be viewed as a gland by which carbonic acid is excreted; the carbonic acid, however, not being formed by the lungs, but simply eliminated by their action. It appears, therefore, that those organs which are destined for the separation of excretions from the body do not form the various substances, but simply eliminate them. The case, however, is otherwise with the glands which furnish substances destined to be consumed subsequently by the economy: these glands in such cases seem to effect a true transformation of the blood, one part of which forms the peculiar matter of the secretion (as for example, sugar of milk in the mammary gland), the other, or complementary portion, is returned into the mass of circulating fluid. The true mechanism of secretion is at present unknown. It has been imagined that secretion may present a certain analogy with the case of vinous fermentation, in which, little as we know of the cause, we understand the conditions requisite to produce it; for it appears that the main point consists in the presence of certain organic molecules, since it is found by the experiment of placing yeast in a tube closed with filtering paper, and dipping it into a solution of syrup (p. 131), that actual contact with those molecules is necessary to produce the decomposition, the liquid in the tube being the only part which ferments: hence we may conceive why blood out of the gland undergoes not the same changes as when circulating through it. No satisfactory attempt has hitherto been made to explain why one substance should produce one kind of decomposition, and a different substance a totally different decomposition, although the compound operated on be the same in both cases.

CHAPTER XIV.

§ I. Atomic Volumes. § II. Atomic Heat. § III. Heat of Combination.

(1514) Having now completed our survey of the different classes of organic compounds, we may proceed in the last place to review briefly some points connected with the theory of the atomic constitution of matter which could not conveniently be discussed until the chemical properties of the various compounds, both organic and inorganic, had been described.

Two theories of the composition of material bodies have been maintained with varying degrees of credit from the earliest ages of the Grecian philosophy to the present time: the one founded on metaphysical views: the other, and now the generally received opinion, based on physical considerations.

Upon the first view of the constitution of matter, it is supposed that the particles of which bodies consist are capable of subdivision without limit. Every particle of matter must possess an upper and a lower surface, and therefore it is conceivable that these surfaces may be separated from each other.

The second view, which was upheld, amongst other illustrious men, by Sir Isaac Newton, maintains that though matter is susceptible of subdivision into molecules of inconceivable minuteness, there is a point beyond which no power within the reach of man, whether mechanical or chemical, can carry this reduction, and these particles are hence appropriately termed *atoms* (or indivisibles). This view has acquired great additional probability since the phenomena of chemical combination have been better understood and more accurately examined. Upon this *atomic* hypothesis, as now generally admitted, it is supposed that the particles of which each element consists, have a definite and uniform size, the atom being the smallest quantity of any substance which is capable of existing in combination with other particles (918).

The phenomena of chemical combination, and the laws of definite, multiple, and equivalent proportion, as well as the existence of polymeric and metameric compounds, indeed admit of a simple explanation by the aid of this hypothesis, which as developed by Dalton, has received the name of the *atomic theory*.

Dalton assumes that the ultimate particles of any given element are of uniform size, and possess the same relative weight; but that the particles of different elements differ from each other in weight, and possibly also in size. When chemical combination takes place between any two elementary bodies, combination is supposed to occur between them atom to atom. Hence the proportions in which bodies unite must of necessity be definite and invariable. In like manner the law of multiple proportion becomes a physical necessity, since compounds must be formed by the union of 1 atom of one of the elements with 1, 2, 3, 4, or more atoms of the other element; or 2 atoms of one element with 1, 3, 5, or 7 atoms of the other (922).

The combining numbers of the different elements simply express the relative weights of their atoms, and hence the term *atomic weight* is by many writers used as synonymous with that of *chemical equivalent* (13), or *combining proportion*.

Nothing is known of the absolute size or weight of these ultimate particles of matter, but it appears to be certain that the amount of heat, of electricity, and of other forces associated with each chemical atom, is perfectly definite. We are also in ignorance of the form of these atoms, for it is clearly proved that the minutest particle of matter which the eye, assisted by the most powerful microscope, is able to perceive, yet consists of an indefinite multitude of atoms: the configuration of such minute visible particles cannot therefore furnish any clue to the shape of the ultimate particles of which the body is composed. It is, however, not improbable that the atoms of the elementary bodies are either spherical or spheroidal; the simplicity of such forms being most in harmony with the equality of attraction in different directions.

§ I. ATOMIC VOLUMES.

(1515) Various attempts have been made to determine the relative sizes of the atoms of different elements, some of which will be briefly noticed almost immediately. It is probable that, even in solids, the distances between their component particles are much greater than the diameters of the particles themselves; and in gaseous bodies these intervals of course will be very much greater than in liquids or in solids. The observations of Dalton and of Gay-Lussac upon the effects of temperature upon gases led these philosophers to the conclusion that the expansion and contraction which aëriform bodies undergo when subjected to equal increments or decrements of temperature, *cæteris paribus*, is uniform; and it has hence been argued, from the results obtained by Gay-Lussac, and by Dalton, that in aëriform substances the relative distances between the component particles of all gases must be uniform in all. More accurate researches have, however, shown that, although for general purposes the law of the uniformity of expansion of gases by heat may be admitted, yet it is not absolutely true, and that the departure from this law is particularly evident in the case of those vapours and gases which are readily liquefied by pressure (*note*, p. 186, Part 1.). Experiment has proved, that in the case of elementary bodies which are in the gaseous form, the equivalent quantities of these bodies are proportionate to their densities, as shown in the table given on the following page, and the equivalents of these elements are consequently represented by numbers which exhibit the ratio of their atomic weights.

Oxygen, phosphorus, arsenic, sulphur, and selenium form exceptions to this rule. Gerhardt, however, induced by other considerations, doubles the usual atomic weight of oxygen and of sulphur, in favour of which procedure strong arguments may be adduced (919). If his view be adopted, the anomaly disappears in the case of oxygen, and some of the other exceptions may be explained, by admitting that in such instances the repulsive power of heat may be insufficient to cause the complete resolution of a body into its ultimate atoms; that in phosphorus, and in arsenic, for example, two of these atoms may remain associated together, whilst in the case of sulphur not less than six atoms (or three atoms if Gerhardt's view be followed) may be so associated; inasmuch as instances occasionally occur, as in the case of copper and mercury, in which two atoms of a substance combine as one, so that such a supposition is not in contradiction to known analogies. At a temperature below 1500° an equivalent of sulphur yields a volume of vapour equal only to one-third of that of one equivalent of oxygen at the same temperature; but if heated beyond 1800° it becomes dilated, till it occupies the same bulk as an equivalent of oxygen similarly heated. Selenium also exhibits an anomalous difference in the density of its vapour at low and at high temperatures, similar to that observed in the case of sulphur, and though as yet no indications of any corresponding abnormal increase in the rate of expansion has been observed with phosphorus or arsenic, there is nothing improbable in the supposition that, at temperatures still more elevated than those hitherto tried, results analogous to those obtained with sulphur and selenium might be procured.

In compound gases it might be supposed that the increased bulk occupied by the compound atom would interfere with the regularity of their expansion, but the bulk of solid matter in any gas is so small compared with the entire space which it occupies, that no sensible irregularity due to this cause is perceptible.

Specific Gravity and Combining Volume of the Elementary Gases.

1 eqt. in grains of the under-mentioned elements yields in cub. in.			Comb. vol.	Specific gravity.		Name of observer.
Grs.		Cb. In.		Calculated.	Observed.	
8	Oxygen . . .	23·33	1		1·10563	Regnault
31	Phosphorus .	23·33	1	4·284	4·4200	Dumas
75	Arsenic . . .	23·33	1	10·1670	10·6000	Mitscherlich
16	Sulphur at 1900°	23·33	1	2·2168	2·2	Deville & Troost
39·7	Selenium 1900°	23·33	1	5·486	6·37	Deville & Troost
16	Sulphur . .	7·77	$\frac{1}{3}$	6·6337	6·617	Dumas
1	Hydrogen . .	46·66	2	0·0691	0·0692	Regnault
14	Nitrogen . .	46·66	2	0·9674	0·9713	Regnault
35·5	Chlorine . .	46·66	2	2·4531	2·47	Gay-Lussac
80	Bromine . .	46·66	2	5·5281	5·54	Mitscherlich
127	Iodine . . .	46·66	2	8·756	8·716	Dumas
56·0	Cadmium . .	46·66	2	3·869	3·94	Deville & Troost
100	Mercury . .	46·66	2	6·9101	6·976	Dumas

The third column of this table indicates the bulk of vapour in cubic inches, furnished by a number of grains of each element corresponding to its combining number, the values in each case being calculated at a temperature of 60°, and under a barometric pressure of 30 inches of mercury.

(1516) *Atomic Volume of Compound Gases.*—Allusion has been already made (14) to the important law of combination—viz., that when two gaseous substances unite, the bulk of the resulting compound, if gaseous or vaporous, when it does not coincide with the united bulk of its components, yet always bears a simple relation to it. The two gases after combination never occupy a larger volume than they did when separate. No fixed rule, however, can be laid down by which it can be predicted whether condensation will occur; or, if it occur, what will be the amount of condensation that will accompany the act of combination. In the majority of instances where equal volumes of the component gases unite, as in the acids containing hydrogen, no change of volume takes place. Numerous cases, nevertheless, exist where, as in the compounds of mercury, equal volumes of different gases or vapours in uniting become condensed to one-half of their former bulk. When two volumes of one gas unite with one of a second, the condensation is generally found to be in such a proportion that the three volumes after combination occupy the space of two. This is exemplified by the protoxides of nitrogen, of chlorine, and of hydrogen, and the probability that such is also the case with carbon has led to the adoption of two volumes of vapour as the representative of the atom of carbon. Such a mode of condensation, however, is not uniform. In some cases the three volumes are condensed into one, as in cyanogen, and in light carburetted hydrogen gas; whilst in the complex molecules of organic chemistry the condensation is much greater. The following Table comprises the determination of the vapour-density of the principal substances described in the Second Part of this work, and it exhibits the degree of condensation in each case:—

Table showing the Density of several Compound Gases and Vapours.

Name.	Constituents.		Formulæ.	Density.			Authority.
				Calculated. H = 1.	Calculated Air = 1.	Observed. Air = 1.	
1. *Gases united without Condensation.*							
	vols.	vols.					
Hydrochloric acid . .	2 H	2 Cl	$\frac{HCl}{4}$	18·2	1·2611	1·2474	Biot and Arago
Hydrobromic acid. . .	2 H	2 Br	$\frac{HBr}{4}$	40·5	2·7986	2·71	Lowig
Hydriodic acid	2 H	2 I	$\frac{HI}{4}$	64·0	4·4125	4·443	Gay-Lussac
Hydrocyanic acid. . .	2 H	2 Cy	$\frac{HCy}{4}$	13·5	0·934	0·9476	Gay-Lussac
Deutoxide of nitrogen .	2 N	2 O	$\frac{NO_2}{4}$	15	1·038	1·0389	Bérard
Muriate of Ammonia .	4 H_3N	4 HCl	$\frac{H_4NCl}{8}$	13·4	0·9259	0·89	Bineau
Hydriodate of phosphuretted hydrogen . .	4 H_3P	4 HI	$\frac{H_4PI}{8}$	40·5	2·798	2·77	ditto
Hydrobromate do. .	4 H_3P	4 HBr	$\frac{H_4PBr}{8}$	28·7	1·983	1·906	ditto
3 *Volumes condensed into* 2.							
Steam . . .	4 H	2 O	$\frac{H_2O_2}{4}$	9	0·6220	0·6235	Gay-Lussac
Protoxide of nitrogen .	4 N	2 O	$\frac{N_2O_2}{4}$	22	1·5241	1·5200	Colin
Hypochlorous *anhydride* .	4 *Cl*	2 *O*	$\frac{Cl_2O_2}{4}$	43·5	2·9870		

Table showing the Density of several Compound Gases and Vapo

[*Continued.*]

Name.	Constituents.		Formulæ.	Density.			Author
				Calculated. H = 1.	Calculated Air = 1.	Observed. Air = 1.	
	vols.	vols.					
Peroxide of chlorine .	2 Cl	4 O	$\frac{ClO_4}{4}$	33·8	2·331	2·322	Gay-Lu
Peroxide of nitrogen .	2 N	4 O	$\frac{NO_4}{4}$	23	1·592	1·720	Mitsche
Calomel . .	4 Hg	2 Cl	$\frac{Hg_2Cl}{4}$	117·7	8·136	8·350	ditto
Dibromide of mercury .	4 Hg	2 Br	$\frac{Hg_2Br}{4}$	140	9·674	10·140	ditto
*Carbonic oxide	4 C ?	2 O	$\frac{C_2O_2}{4}$	14	0·9674	0·967	Wrede
†Sulphuretted hydrogen .	4 H	2 S	$\frac{H_2S_2}{4}$	17	1·174	1·1912	Gay-Lu
Seleniuretted hydrogen .	4 H	2 Se	$\frac{H_2Se_2}{4}$	40·7	2·8213	2·795	Binea
Telluretted hydrogen .	4 H	2 Te	$\frac{H_2Te_2}{4}$	65·5	4·526	4·489	Calcul
Sulphurous acid	2 S	4 O	$\frac{S_2O_4}{4}$	32	2·2112	2·247	Berzeliu
Selenious acid	2 Se	4 O	$\frac{Se_2O_4}{4}$	55·7	3·8419	4·03	Mitscher
Carbonic acid	4 C_2O_2	2 O	$\frac{C_2O_4}{4}$	22	1·5203	1·529	Regnault
Sulphuric acid	4 S_2O_4	2 O	$\frac{S_2O_6}{4}$	40	2·764	3·01	Mitscher
			4 Volumes condensed into 2.				
Corrosive sublimate	2 Hg	2 Cl	$\frac{HgCl}{2}$	135·5	9·363	9·800	Mitscher
Bromide of mercury .	2 Hg	2 Br	$\frac{HgBr}{2}$	180	12·438	12·160	ditto
Red iodide of mercury .	2 Hg	2 I	$\frac{HgI}{2}$	227	15·666	15·600	ditto
Chlorocarbonic acid .	4 C_2O_2	4 Cl	$\frac{C_2O_2Cl_2}{4}$	49·5	3·420	3·6808	J. Davy
Ammonia . .	6 H	2 N	$\frac{H_3N}{4}$	8·5	0·5896	0·590	H. Davy
Bisulphide of carbon . .	4 S ?	4 C	$\frac{C_2S_4}{4}$	38	2·6260	2·6447	Gay-Lus
Chlorosulphuric acid	4 S_2O_4	4 Cl	$\frac{S_2O_4Cl_2}{4}$	67·5	4·664	4·703	Regnault
Dutch liquid .	4 C_4H_4	4 Cl	$\frac{C_4H_3Cl, HCl}{4}$	49·5	3·420	3·478	ditto
Monochlorinated do.			$\frac{C_4H_2Cl_2, HCl}{4}$	66·7	4·613	4·613	ditto

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* Here it is assumed that 1 equivalent of carbon yields 2 volumes of vapo
Many chemists consider that it yields only 1 volume.

† Sulphur, in accordance with Bineau's researches upon it at high te
peratures, is assumed to have an equivalent volume equal to that of oxyge
and selenium and tellurium are supposed to be analogous to it.

ing the Density of several Compound Gases and Vapours.

[*Continued.*]

Constituents.	Formulæ.	Density. Calculated. H = 1.	Density. Calculated. Air = 1.	Density. Observed. Air = 1.	Authority.
	$\frac{C_4HCl_3,HCl}{4}$	84·0	5·804	5·767	Regnault
	$\frac{C_4Cl_4,HCl}{4}$	101·25	6·996		
	$\frac{C_4Cl_4,Cl_2}{4}$	118·5	8·188	8·157	ditto
4 S ? 4 Cl	$\frac{S_4Cl_2}{4}$	67·5	4·644	4·70	Dumas
2 B ? 6 F ?	$\frac{BF_3}{4}$	33·9	2·345	2·312	ditto
7 Volumes condensed into 4.					
6 H 1 P	$\frac{H_3P}{4}$	17	1·175	1·185	ditto
6 H 1 As	$\frac{H_3As}{4}$	39	2·748	2·695	ditto
5 Volumes condensed into 3.					
4 Cl 6 O	$\frac{Cl_2O_6}{6}$	39·7	2·740	2·6461	Millon
5 Volumes condensed into 2.					
4 C ? 6 Cl	$\frac{C_2Cl_3}{4}$	59·25	4·094	4·082	Regnault
4 Fe ? 6 Cl	$\frac{Fe_2Cl_3}{4}$	162·5	11·223	11·39	Deville & Troost
4 Al ? 6 Cl	$\frac{Al_2Cl_3}{4}$	133·9	9·252	9·34	ditto
4 Al ? 6 Br	$\frac{Al_2Br_3}{4}$	267·5	18·483	18·6	ditto
4 Al ? 6 I	$\frac{Al_2I_3}{4}$	408·5	28·227	27·0	ditto
6 Volumes condensed into 2.					
8 C ? 4 N	$\frac{C_4N_2}{4}$	26	1·800	1·8064	Gay-Lussac
4 C ? 8 Cl	$\frac{C_2Cl_4}{4}$	77	5·320	5·3	Regnault
4 C ? 8 H	$\frac{C_2H_4}{4}$	8	0·552	0·557	Thomson
4 Ti ? 8 Cl	$\frac{Ti_2Cl_4}{4}$	96	6·633	6·836	Dumas
4 Zr ? 8 Cl	$\frac{Zr_2Cl_4}{4}$	115·8	8·002	8·15	Deville & Troost
4 Sn ? 8 Cl	$\frac{Sn_2Cl_4}{4}$	130	8·98	9·199	Dumas

vapour volume of one atom of each of the different metals is assumed

Table showing the Density of several Compound Ga

[*Continued.*]

Name.	Constituents.	Formulæ.	Density. Calculated. H = 1.	Calculated. Air = 1.
Fluoride of silicon .	4 Si ! 8 F !	$\frac{Si_2F_4}{4}$	52	3·587
Chloride of silicon . .	4 Si ! 8 Cl	$\frac{Si_2Cl_4}{4}$	85	5·873
Chlorochromic acid .	4 Cr ! 4 O, 4 Cl	$\frac{Cr_2O_4Cl_2}{4}$	77·8	5·376
		7 Volumes condensed into 2.		
Terchloride of phosphorus	1 P 6 Cl	$\frac{PCl_3}{4}$	68·7	4·713
Terchloride of arsenic	1 As 6 Cl	$\frac{AsCl_3}{4}$	90·7	6·184
Terchloride of antimony	1 Sb 6 Cl	$\frac{SbCl_3}{4}$	114·2	7·894
Terchloride of bismuth	1 Bi 6 Cl	$\frac{BiCl_3}{4}$	158·5	10·934

In the foregoing Table all compounds into th
which carbon and hydrogen both enter are represent
weight equal to 4 volumes of vapour, (O=8 being
and in the majority of other cases the formulæ g
volume formulæ. This, indeed, appears to be the
of bodies in the aeriform state.

Exceptions, however, occur in the case of the s
the hydrochlorate, hydrobromate, hydrocyanate,
sulphate of the sulphide furnish 8 volumes of vap
endeavoured to explain this anomaly on the sup
the high temperature necessary to volatilize these
position takes place, and the salt is resolved into its
ammonia and the gaseous acid; and as the tempe
enter again into combination. This view is inge
also applicable to a case such as that of the h
ammonia H_4NS, which yields a 6-volume vapou
be produced by the separation of the compoun
stituents ammonia (4 vols.) and sulphuretted hydr

Similar explanations have been suggested
hydriodate and hydrobromate of phosphuretted
molecule of each of which yields 8 volumes of vapo

---

to correspond with that of an atom of hydrogen, and
double that of the atom of oxygen; and the same assump
case of silicon and of boron.

carbonate of ammonia $H_4NO,H_2NC_2O_3$, according to the observation of Bineau, yields 12 volumes of vapour; and this would be the result if it broke up into 2 H_3N=8 vols., and C_2O_4 4 vols.

In like manner Regnault observed that the compound $C_4Cl_6O_4$, obtained by acting with chlorine upon methylic ether, yields 8 vols. of vapour, which may be explained on the supposition that when heated it splits into phosgene $C_2Cl_2O_2$ (4 vols.), and bichloride of carbon C_2Cl_4, also 4 vols.

Pentachloride of phosphorus is also a body which yields 8 vols. of vapour, and which, at high temperatures, it has been suggested may be resolved into terchloride of phosphorus, PCl_3 (4 vols.), and chlorine (Cl_2), also 4 vols.

There are, however, cases in which such an explanation is inadmissible. Chlorous anhydride $(ClO_3)_2$ is a 6-volume gas at ordinary temperatures; but it is clear that it is a true combination, and not a mixture of chlorine and oxygen.

Orcin, to which, in its anhydrous condition, the formula ($C_{14}H_8O_4$) is assigned, yields a 3-volume vapour (Dumas); but this, if correct, cannot be explained upon Kopp's theory.

Some remarkable irregularities have been observed in the volume occupied by the vapours of many volatile compounds. Many of these vapours at a low temperature have a density much greater than that which they possess when more strongly heated. The vapours of the volatile acids, such as the formic and the acetic acids in particular, exhibit this anomaly in a marked degree (1103).

(1517) *Atomic Volumes of Solids.*—1. *Simple Bodies.*—It has been supposed that if the atoms of all the elementary bodies were of the same size, the specific gravities of the bodies in their solid form would be in the same proportion as their atomic weights. In such a case, however, either the particles composing the solid must be in actual contact, or the intervals between the particles must be equal. Dumas showed many years ago that the specific gravity of certain isomorphous metals was nearly in the direct ratio of their atomic weights. Since then both Schröder and Kopp have pointed out a number of remarkable relations between the densities of different bodies and their atomic weights. Kopp has shown that many of the elementary bodies may be arranged in groups, each group consisting of members in which the atomic volume is identical. If such weights of the different elementary bodies as represent the atomic weights of each be compared together, the bulk occupied by each body will be such as is indicated in the column headed *atomic volume* in the following Table:—

Table of the Atomic Volumes of Elementary Bodies.

Names of elements.	Equiv. No.		Atom. vol.		Calculated sp. gr.*	Observed specific gravity.
	O=100.	H=1.	O=100.	H=1.		
Carbon	75	6	22	1·76	3·41	3·55, 3·336, (diamond) Jacquelain
Glucinum	58·3	4·66	26·8	2·22	2·1	2·1, Debray
Cobalt	369	29·5	43·3	3·47	8·50	8·49, Brunner; 8·51, Berzelius; 8·95, Rammelsberg
Copper	395	31·7	44·3	3·55	8·92	8·96, Berzelius; 8·72, Karsten; 8·92, Marchand and Scheerer
Iron	350	28	44·2	3·55	7·84	7·84, Broling; 7·79, Karsten
Manganese	345	27·6	44	3·50	7·94	8·03, Bachmann; 8·01, John
Chromium	328	26·3	44	3·50	7·45	6·81, Wöhler
Nickel	369	29·5	43·3	3·47	8·5	8·40, Tourte; 8·82, Tupputi; 8·60, Brunner
Iridium	1232	98·6	57	4·56	21·6	21·15, Deville and Debray
Osmium	1244	99·4	57	4·56	21·8	21·4, Deville and Debray
Palladium	666	53·2	57	4·56	11·7	11·3—11·8, Wollaston, Deville
Platinum	1232	98·6	57	4·56	21·6	21·0, Borda; 21·5, Berzelius, Wollaston
Rhodium	652	52·2	57	4·56	11·4	11·0, Wollaston; 11·2, Cloud; 12·1, Deville and Debray
Ruthenium	651	52·1	57	4·56	11·4	11·1—11·4, Deville and Debray
Zinc	406	32·5	57	4·56	7·14	7·14, Wertheim; 6·86,—7·21, Berzelius
Aluminum	171	13·7	66	5·28	2·59	2·56—2·67, Deville
Molybdenum	600	48	66	5·28	9·09	8·62—8·64, Bucholz
Tungsten	1150	92	66	5·28	17·4	17·2, Allen; 17·4, Bucholz; 17·6, D'Elhuyart
Cadmium	697	55·7	81	6·48	8·6	8·60, Stromeyer; 8·63, Karsten, Kopp
Magnesium	150	12	86	6·88	1·743	1·743, Bunsen
Mercury	1250	100	91	7·28	13·6	13·6, Kupffer, Karsten; 13·56, Faraday
Selenium	495	39·6	103	8·24	4·8	4·8, Schaffgotsch; 4·30—4·31, Berzelius
Sulphur	200	16	101	8·08	1·99	1·99—2·05, Karsten; 1·99, Breithaupt
Tin	742	59	101	8·10	7·28	7·28, Herapath; 7·29, Kupffer, Karsten
Lead	1294	103·6	114	9·12	11·35	11·44, Berzelius; 11·35, Herapath; 11·33, Kupffer; 11·36, Reich
Gold	2458	196·6	128	10·04	19·2	19·34, G. Rose; 19·26, Brisson
Silver	1350	108	128	10·04	10·53	10·53, G. Rose; 10·4, Karsten
Tellurium	800	64	128	10·04	6·25	6·25, Berzelius
Lithium	87	7	147	11·80	0·593	0·593, Bunsen
Calcium	250	20	158	12·64	1·578	1·578, Bunsen
Arsenic	937	75	162	12·96	5·7	5·7—5·969, Guibourt; 5·67, Herapath
Phosphorus	387	31	211	16·88	1·83	1·83, Schrötter; 1·77, Berzelius
Strontium	550	43·7	216	17·28	2·54	2·54, Bunsen
Antimony	1525	122	227	18·16	6·7	6·71, Marchand and Scheerer; 6·7, Karsten
Bismuth	2625	210	266	21·34	9·84	9·88, Thénard; 9·83, Herapath; 9·8, Marchand and Scheerer
Bromine	1000	80	320	25·6	3·12	(liquid) 2·99, Löwig; 2·97, Balard
Chlorine	443	35·5	320	25·6	1·38	(liquid) (1·33 about), Faraday
Iodine	1587	127	320	25·6	4·95	4·95, Gay-Lussac
Sodium	287	23	295	23·60	0·972	0·972, Gay-Lussac and Thénard
Potassium	487	39	562	44·96	0·865	0·865, Gay-Lussac and Thénard

* In the above Table, the column headed *calculated specific gravity* indicates the numbers which, if used as divisors of the equivalent numbers, yield the numbers which are adopted as the *atomic volume* of the body.

The atomic volume (or specific volume) of any substance, simple mpound, may be calculated by dividing its chemical equivalent s specific gravity. Thus, if $d=$ the density or specific gravity, the atomic weight or chemical equivalent, and $v=$ the atomic ne, $\frac{q}{d}=v$.

A simple mode of determining experimentally the atomic me of a body was employed by Playfair and Joule. Their ratus or *volumenometer* consists of a globular flask provided a long narrow neck, about twelve inches in length, graduated below upwards, to indicate grains of water. The flask is ided with a tubulure (accurately fitted with a ground stopper) the admission of the solid body for experiment. When the rument is to be used it is to be filled up to the mark 0° on the n, with water, with oil of turpentine, or with some liquid ch exerts no solvent action on the body. It is then inclined ne side, the stopper removed, and a weighed quantity of the d under experiment is carefully introduced : the stopper is then aced, and the number of divisions which the liquid is raised the stem indicates in grains the quantity of water which has displaced. Thus, if 350 grains of iron (an equivalent in ns on the oxygen scale) be introduced, the liquid will rise divisions in the stem of the instrument, indicating the valent volume by simple inspection. If the quantity of the tance employed be less, say one third, or one fourth of an valent in grains, the rise in the stem, when multiplied by 3 y 4, as the case may be, indicates the atomic volume of the under experiment. The same experiment also furnishes the for determining approximatively the specific gravity of the , since the weight of the substance used, when divided by the ber of divisions which the liquid has risen (corresponding to veight of the bulk of water equal to the solid) will, of course, the specific gravity.

Schröder, Kopp, and many of the chemists who have worked this subject, have made their calculations upon the oxygen of equivalents; but recently Kopp and others have adopted lations from the hydrogen unit; both sets of numbers are efore given in the Table to facilitate reference.

From the foregoing Table, it is apparent that several groups *ometric* elementary bodies (that is to say, bodies possessed of l atomic volume), exist; and that between many of these groups, iple relations of a simple kind occur, thus :—

1. The *atomic volume of* the group containing cobalt, copper,

iron, manganese, and nickel, is double that of carbon as found in the diamond.

2. The atomic volume of the group containing aluminum, molybdenum, and tungsten, is to that of the iron group as 2 : 3.

3. The atomic volume of lead is double that of platinum and its congeners.

4. There are indications of an equality in the atomic volume of the halogens—chlorine, bromine, and iodine; but the specific gravities of these bodies are not known with sufficient accuracy to admit of a satisfactory comparison. That of chlorine is only an approximation, and it was in the liquid form, whereas, iodine, with which it is compared, was in the solid state.

5. It has been supposed that the atomic volume of potassium is double that of sodium; but if this be so, the specific gravities of the two metals obtained by experiment must be inaccurate. If that of sodium were 0·99, and that of potassium 0·84, the ratio of their atomic volumes would be as 290 : 580, or as 23·2 : 46·4.

(1518) *Influence of Isomorphism and of Dimorphism on Atomic Volume.*—Kopp has further shown that the coincidence in atomic volume first observed by Dumas in the case of certain isomorphous metals, holds good very generally with isomorphous bodies; so that, when the volumes occupied by equivalent weights of such bodies are compared together, the volumes, allowing for errors of observation, are identical. This law is found to hold good both with elementary and with compound bodies.

A close approach to isomorphism in compound bodies does not, however, necessarily indicate the isomorphism of all their corresponding constituents. Sulphate of zinc, for example, is isomorphous with sulphate of iron, but metallic zinc and metallic iron are not isomorphous; and indeed, strictly speaking, the salts are not identical in form, for though the crystals resemble each other in their geometrical figure, yet when their angles are accurately measured, considerable differences are detected. The solid volume of the crystallized sulphates of zinc and of iron differs but little; the atomic volume of sulphate of zinc, according to Filhol's experiments, being 880, and that of sulphate of iron 920, and since so large a proportion of the mass of the salt is in each case made up by substances which are identical, the same general form is preserved in both salts.

In the case of dimorphous substances, the specific gravity of the body in one of its forms is greater than it is in the other form; consequently, such substances possess two different atomic nes. The following Table contains the specific gravity and ic volume of a few dimorphous substances:—

Dimorphous bodies.	Specific gravity.	Atomic volume.
Diamond	3·41	22
Graphite	2·09	36
Native sulphur (octohedral)	2·05	97·5
Prismatic sulphur . . .	1·98	101
Viscous sulphur	1·957	102
Iceland spar	2·72	229
Aragonite	3·00	211

(1519) *Disturbing Influence of Temperature.*—There can be no bt that the atomic volume of a body is a character as definite its specific gravity, or its equivalent number; but the determion of its precise amount is opposed by some peculiar and iderable obstacles. One of these arises from the difficulty ccurately determining the specific gravity of a solid, under cirstances which shall be properly comparable. Since the bulk l bodies varies with the temperature, and increases as the temture rises, the specific gravity, as taken in the ordinary method, be liable to variation according to the temperature. This d be of little consequence, however, if the amounts of expanproduced by equal increments of heat were alike in all bodies; experiment distinctly proves that this is not the case, and the t extent of this variation amongst many of the simple bodies, be seen by the subjoined Table:—

Cubic Expansion of some of the Metals from 32° to 212°.

letal.	Equal bulks.		Atomic volumes.		Approximative ratio of expansion for at. vols.		Authority.
	parts at 32°,	gain at 212°,	parts at 32°,	gain at 212°,			
n .	100	0·354	44	0·147	1	0·150	Dulong and Petit.
tinum	100	0·264	57	0·150			
pper	100	0·515	44	0·226	1·5	0·225	Lavoisier and Laplace.
ic .	100	0·882	57	0·332	2	0·300	Smeaton.
ld .	100	0·440	128	0·582	4	0·600	Lavoisier and Laplace.
. .	100	0·581	101	0·586			Do.
timony	100	0·325	227	0·737	5	0·750	Smeaton.
ver .	100	0·573	128	0·733			Lavoisier and Laplace.
ad .	100	0·854	114	0·974	6·5	0·975	Do.
muth	100	0·417	270	1·126	7·5	1·125	Smeaton.
rcury	100	1·802	91	1·640	11	1·650	Dulong and Petit.

[illegible]

[illegible]

[illegible]

[illegible] may be equally well explained upon the older view, [illegible] for I have found by a very slight [illegible] of one of the values for sulphuric acid, that numbers [illegible] with which the results of experiment accord quite as well as with the numbers assumed by Kopp, as will be seen almost immediately.

The oxides may be subdivided into four classes, in each of which the oxygen must be supposed to undergo a different amount of condensation. In the first class, the equivalent volume of oxygen is assumed by Kopp to be 16, the metal retaining its original volume; in the second and more numerous class, the metal retains its original volume, but that of oxygen is 32; in the third class the volume of oxygen is 64. In the fourth class, assuming the volume of oxygen to be 32, the metals undergo condensation in the act of combining:

thus, I find that aluminum, calcium, and strontium are condensed into exactly half their volume. The specific gravity of barium is not known with certainty, but it is probable that it likewise belongs to the same class. The condensation experienced by sodium and by potassium is such, that they occupy very nearly one third of the volume which they possess in the uncombined form; thus, if the atomic volume of these two metals be divided by 3, we have for sodium 293÷3=98; by observation of the density of soda, it is =102, when combined with oxygen of an atomic volume of 32; and for potassium, 562÷3=187; whilst by observation of the density of potash it is 184.

The tables which follow are based upon those given by Kopp, but they include many new data, and several of the results have been re-calculated from the values more recently assigned to the atomic weights of iron, antimony, calcium, chromium, mercury, molybdenum, tungsten, and zinc. The atomic volumes for the various salts are all calculated, not on the binary theory, but on the hypothesis that the salts consist of an oxide united with an anhydrous acid.

Atomic Volumes of certain Oxides.

Oxide.	Formula.	Eqt. No. O=100	Calculated Atomic Volume.	Calcul. Sp. gr.	Observed Specific Gravity.
			CLASS I. Volume of O=16.		
Antimony	SbO_4	1925	227+ 64=291	6·61	6·53, Boullay; 6·70, Karsten.
Chromium	Cr_2O_3	956	132+ 48=180	5·31	5·21, Wöhler.
Tin	SnO_2	935	101+ 32=133	7·03	6·96, Mohs; 6·90, Boullay; 6·64, Herapath.
			CLASS II. Volume of O=32.		
Cadmium	CdO	797	81+ 32=113	7·05	6·95, Karsten.
Copper	CuO	496	44+ 32= 76	6·53	6·43, Karsten; 6·15, Boullay; 6·4, Herapath; 6·322, Filhol.
Lead	PbO	1394	114+ 32=146	9·55	9·50, Boullay; 9·361, Filhol.
Mercury	HgO	1350	91+ 32=123	10·97	11·0, Boullay; 11·1, Herapath; 11·19, Karsten.
Silver	AgO	1450	128+ 32=160?	9·06	8·26, Karsten; 7·25, Boullay.
Tin	SnO	835	101+ 32=133	6·28	6·67, Herapath.
Zinc	ZnO	506	57+ 32= 89	5·68	5·43, Mohs; 5·60, Boullay; 5·73, Karsten.
Cobalt	Co_2O_3	1037	88+ 96=184	5·63	5·60, Boullay; 5·32, Herapath.
Iron	Fe_2O_3	1000	88+ 96=184	5·43	5·23, Boullay; 5·25, Mohs.
Antimony	SbO_3	1825	227+ 96=323	5·65	5·78, Boullay; 5·57, Mohs.
Bismuth	BiO_3	2960	270+ 96=366	8·09	8·17, Karsten; 8·21, Herapath; 8·45, Dumas.
			CLASS III. Volume of O=64.		
Copper	Cu_2O	892	88+ 64=152	5·87	5·75, Karsten, Dumas; 6·05, Herapath.
Mercury	Hg_2O	2600	182+ 64=246	10·56	10·69, Herapath; 8·95, Karsten.
Molybdic acid	MoO_3	900	66+192=258	3·48	3·46, Bergmann; 3·49, Berzelius.
Tungstic acid	WO_3	1450	66+192=258	5·62	5·27, Herapath; 6·12, Berzelius.

Oxides, Class IV., *in which the metal undergoes condensation.* O=32.

Oxide.	Formula.	Eqt. No. O=100.	Calculated Atomic Volume.	Calcul. Sp. gr.	Observed Specific Gravity.
Alumina. .	Al_2O_3	642	66+ 96=162	3·96	4·154, Filhol; 3·95 (ruby).
Baryta . .	BaO	958	143+ 32=175	5·47	5·456, Filhol.
Lime. . .	CaO	350	79+ 32=111	3·15	3·18, Filhol, Boullay; 3·08, Lěroyer and Dumas.
Potash . .	KO	587	184+ 32=216	2·71	2·66, Karsten.
Soda . . .	NaO	387	102+ 32=134	2·88	2·87, Karsten.
Strontia . .	SrO	650	108+ 32=140	4·64	4·611, Fihol.

Kopp divides the chlorides into two classes, in one of which he supposes the volume of the chlorine to be 196, and the other 245, the ratio of these volumes in the two classes being as 4 : 5. The accordance between the observed and the calculated results in these salts is less satisfactory than in the case of the oxides, and it becomes necessary to assume new volumes for those metals which, like potassium, sodium, calcium, and magnesium, undergo condensation in the act of combining: the volumes thus assumed for them, however, exhibit no simple relation to the volume of these metals in an uncombined state :—

Chlorides, Class I. Volume of Cl=196.

Chloride.	Formula.	Equivalent.	Atomic Volume.	Calcul. Sp. gr.	Observed Specific Gravity.
Silver . .	AgCl	1793	128+196=324	5·53	5·5—5·57, Karsten; 5·55, Boullay.
Lead. . .	PbCl	1736	114+196=310	5·60	5·68—5·80, Karsten.
Barium . .	BaCl	1301	143+196=339	3·83	3·86, Boullay; 3·75, Filhol; 3·7 Karsten.
Sodium . .	NaCl	731	130+196=326	2·24	2·26, Mohs; 2·15, Kopp; 2·24, Filhol; 2·08, Karsten; 2·011, Playfair and Joule.
Chlorides, Class II. Volume of Cl=245.					
Cobalt . .	CoCl	812	44+245=289	2·81	2·937; Playfair and Joule.
Copper . .	Cu_2Cl	1237	88+245=333	3·71	3·68, Karsten; 3·376, Playfair and Joule.
Copper . .	CuCl	840	44+245=289	2·90	3·054, Playfair and Joule.
Iron . . .	FeCl	793	44+245=289	2·74	2·528, Filhol.
Mercury	HgCl	1693	91+245=336	5·04	5·14, Gmelin; 5·42, Boullay; 5·40, Karsten.
	Hg_2Cl	2943	182+245=427	6·90	6·99, Karsten; 6·71, Herapath; 7·14, Boullay.
Ammonium	H_4NCl	668	218+245=463	1·44	1·50, Kopp; 1·53, Mohs; 1·578, Playfair and Joule.
Calcium. .	CaCl	693	60+245=305	2·27	2·21—2·27, Boullay; 2·24, Filhol; 2·485, Playfair and Joule.
Magnesium	MgCl	593	40+245=285	2·08	2·177, Playfair and Joule.
Potassium .	KCl	932	234+245=479	1·94	1·994, Filhol; 1·94, Kopp; 1·9 Karsten; 1·90, Playfair and Joule.
Strontium .	SrCl	989	108+245=353	2·80	2·80, Karsten; 2·96, Filhol.

Similar relations have been observed with the various sulphides, but the accordance of theory with observation is still less perfect in these cases, owing partly, perhaps, to the dimorphism of sulphur, and to the impossibility of ascertaining which modification of this element may be present in the compound.

The sulphates are regarded by Kopp as consisting of M,SO_4. They are subdivided by him into two classes: in the first class, SO_4 is assumed to possess a volume = 186, in the second, a volume = 236. There is no simple relation between these two numbers; but if we view the sulphates as formed upon the plan MO,SO_3, and deduct from the numbers assigned by Kopp for SO_4, 32 as the atomic volume of an equivalent of oxygen (adding it in all cases to the numbers which represent the atomic volume of the metal in the salt); the numbers which represent SO_3 in the two classes will be 154 and 204. Now by substituting 153 for 154, we may represent the two volumes of SO_3 by numbers which are in the ratio of 3 : 4, and if this slight alteration be adopted, the atomic volumes obtained by calculation agree as well with those furnished by experiment as those which have been calculated by Kopp.

In the chromates, the tungstates, the carbonates, and the nitrates, but a single class has been recognised for each acid:—

		SULPHATES, CLASS I. $SO_3 = 153$.		
Name of Salt. (Formula MO,SO_3)	Eqt. No. O=100.	Calculated Atomic Volume.	Calcul. Sp. gr.	Observed Specific Gravity.
Lead . . .	1895	146 + 153 = 299	6·32	6·30, Mohs, Filhol; 6·17, Karsten.
Baryta . .	1458	175 + 153 = 328	4·44	4·45, Mohs; 4·20, Karsten.
Potash . .	1087	266 + 153 = 419	2·59	2·62, Karsten, Filhol; 2·66, Kopp; 2·64, Playfair and Joule.
Strontia . .	1148	140 + 153 = 293	3·92	3·59, Karsten; 3·77, Filhol; 3·95, Breithaupt.
		SULPHATES, CLASS II. $SO_3 = 204$.		
Copper . .	997	76 + 204 = 280	3·56	3·53, Karsten, Filhol; 3·631, Playfair and Joule.
Silver. . .	1950	160 + 204 = 364	5·35	5·34, Karsten; 5·41, Filhol; 5·322, Playfair and Joule.
Zinc . . .	1006	89 + 204 = 293	3·43	3·40, Karsten, Filhol; 3·681, Playfair and Joule.
Lime . . .	850	92 + 204 = 296	2·89	2·93, Karsten; 3·102, Filhol; 2·96, Naumann.
Magnesia. .	750	72 + 204 = 276	2·71	2·61, Karsten; 2·628, Filhol; 2·706, Playfair and Joule.
Soda . . .	888	162 + 204 = 366	2·42	2·63, Kopp; 2·629, Filhol; 2·597, Playfair and Joule.
MO,CrO_3.		CHROMATES, $CrO_3 = 196$.		
Lead . . .	2022	146 + 196 = 342	5·91	5·95, Breithaupt; 6·00, Mohs; 5·653, Playfair and Joule.
Potash . .	1215	266 + 196 = 462	2·63	2·64, Karsten; 2·74, Kopp; 2·682, Playfair and Joule.
Silver. . .	2078	160 + 196 = 356	5·83	5·77, Playfair and Joule.
MO,WO_3.		TUNGSTATES, $WO_3 = 212$.		
Lead . . .	2844	146 + 212 = 358	7·94	8·0, Gmelin; 8·1, Leonhard.
Lime . . .	1800	92 + 212 = 304	5·92	6·04, Karsten; 6·03, Meissner.

		CARBONATES, $CO_2 = 119$.		
Name of Salt. (Formula MO,CO_2)	Eqt. No. O = 100.	Calculated Atomic Volume.	Calcul. Sp. gr.	Observed Specific Gravity.
Cadmium .	1073	113 + 119 = 232	4·63	4·42, Herapath ; 4·49, Kopp.
Iron . . .	725	76 + 119 = 195	3·72	3·829, Mohs ; 3·872, Naumann.
Lead . . .	1670	146 + 119 = 265	6·30	6·43, Karsten ; 6·47, Breithaupt.
Manganese .	722	76 + 119 = 195	3·70	3·55—3·59, Mohs.
Silver . . .	1725	160 + 119 = 279	6·18	6·08, Karsten.
Zinc . . .	781	89 + 119 = 208	3·75	4·44, Mohs ; 4·4—4·5, Naumann.
Baryta . .	1233	175 + 119 = 294	4·19	4·30, Karsten, Mohs ; 4·24, Breithaupt ; 4·565, Filhol.
Lime . . .	625	92 + 119 = 211	2·96	3·00 (Aragonite), Breithaupt ; 2·93, Mohs ; 2·70 (Iceland spar), Karsten ; 2·72, Beudant.
Magnesia .	525	72 + 119 = 191	2·75	2·81, Breithaupt ; 3·0—3·11, Mohs.
Potash . .	862	266 + 119 = 385	2·24	2·26, Karsten ; 2·267, Filhol ; 2·103, Playfair and Joule.
Soda . . .	662	162 + 119 = 281	2·38	2·47, Karsten ; 2·509, Filhol ; 2·427, Playfair and Joule.
Strontia . .	923	140 + 119 = 259	3·56	3·60, Mohs ; 3·62, Karsten.
(MO,NO_5).		NITRATES, $NO_5 = 326$.		
Lead . . .	2069	146 + 326 = 472	4·32	4·581, Filhol ; 4·40, Karsten ; 4·34, Kopp ; 4·316, Playfair and Joule.
Silver. . .	2125	160 + 326 = 486	4·37	4·36, Karsten ; 4·336, Playfair and Joule.
Ammonia .	1000	250 + 326 = 576	1·71	1·74, Kopp ; 1·635, Playfair and Joule.
Baryta . .	1634	175 + 326 = 501	3·26	3·200, Filhol ; 3·19, Karsten ; 3·284, Playfair and Joule.
Lime . . .	1025	92 + 326 = 418	2·45	2·240, Filhol.
Potash . .	1263	266 + 326 = 592	2·12	2·10, Karsten ; 2·06, Kopp ; 2·07, Playfair and Joule.
Soda . . .	1063	162 + 326 = 488	2·19	2·260, Filhol, Karsten ; 2·19, Marx ; 2·20, Kopp ; 2·182, Playfair and Joule.
Strontia . .	1324	140 + 326 = 466	2·84	2·857, Filhol ; 2·84, Karsten ; 2·704, Playfair and Joule.

(1521) 3. *Volumes of Compounds in Solution.*—A series of interesting researches was made a few years ago by Playfair and Joule upon the bulk occupied by the equivalent quantities of different solid compounds, compared with that which they occupy when in solution (*Phil. Mag.*, 1845, vol. xxvii.). Some of these results are included in the Table (page 878), in which they are all referred to the quantity of water in grains which an equivalent in grains of each substance (H = 1) would displace when immersed in water.

The quantity of water displaced is easily calculated by dividing the equivalent number of the substance by its specific gravity. It was in these cases determined experimentally by taking a given weight, say an equivalent in grains, of the substance under trial, and introducing it into the volumenometer, described at page 869.

When known quantities of different salts were brought into solution, and the increase of bulk in the liquid thus produced was ied, it was found—1. That a salt when in solution always less space than it did when in the solid state.—2. That nt quantities of different salts when in solution occupy he same volume, or volumes which are simple multiples or iples of each other.* If 9 (the equivalent volume of water) ned as the standard of comparison, an equivalent of the salts, when dissolved in water, increases the volume of the y 9, or by some multiple of 9. For instance, 87 grains or lent of sulphate of potash in its dry state, displaces 33 f water, but it increases the bulk of the liquid by only 18 easures when in solution; 101 grains of nitrate of potash in l form displace 48 grains of water, but when in solution place 36 grains. In the case of carbonate of potash the ation is still greater; for 69 grains of the solid salt occupy a 39 water grains, and of 9 only when in solution. It is, , necessary to remark that the volume occupied by the en in solution is somewhat influenced by the degree of on of the liquid, the increase of volume being slightly when the solution approaches the point of saturation. was found in the case of cane sugar, that when an equi- f sugar (171 grains) was dissolved in different amounts of he increase in volume of the solution was as follows:—

Sugar.		Water.	Temperature.	Atomic volume in grain measures of water.
1	:	120	60°	99·00
1	:	10	52°	105·09
1	:	1	52°	107·01
3	:	1	52°	108·06

'hat when a salt usually crystallizes with a large proportion r of crystallization, such salt, when reduced to the anhy- ate, may be dissolved in water without increasing its bulk.†

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atomic volume of a salt in solution, however, varies considerably temperature, and increases rapidly as the temperature rises, so that at a particular temperature for each salt that this law holds true. solution volume of an equivalent of each of the following salts is

te of zinc . . . $ZnO, SO_3+7\,Aq$, at 32° $= 56·1$ at 90° $= 63$
magnesia . $MgO,SO_3+7\,Aq$. at „ $= 60·8$ at 85° $= 63$
iron . . . $FeO, SO_3+7\,Aq$. at „ $= 61·0$ at 80° $= 63$.

s observation was originally made by Dalton, but he supposed that es when a salt was dissolved in water, the bulk of the liquid was , except by the bulk of water which the salt might contain.

For example, anhydrous carbonate of soda, and the anhydrous sulphates of soda and of magnesia, may be brought into solution without adding to the bulk of the liquid. If the salts be dissolved in their hydrated form, they increase the bulk of the liquid solely by the number of grains of water of crystallization which they contain: thus 143 grains, or one equivalent in grains of crystallized carbonate of soda, or 161 grains of the crystallized sulphate of soda, each of which contains 90 grains, or 10 equivalents of water of crystallization, causes an increase of 90 grain measures in the bulk of the water in which it is dissolved; 123 grains, or an equivalent of sulphate of magnesia, containing 7 equivalents or 63 grains of water, occasions an increase of 63 grain measures of water when brought into solution.

Volumes in grains of water of an equivalent in grains of several anhydrous salts, both when dry and when in solution (H=1).

Name of the Metal.	Chloride.		Bromide.		Iodide.		Sulphate.		Nitrate.		Carbonate.	
	Dry.	Solution.	Dry.	Solution.	Dry.	Solution.	Dry.	Solution.	Dry.	Solution.	Dry.	Solution.
Potassium	39·3	26·8	44·0	28·8	54·2	44·0	33·0	18·0	48·9	36·1	33·0	9·2
Sodium .	29·2	18·3	...	19·0	...	...	27·5	1·6	39·1	26·5	22·0	0
Ammonium	34·0	35·7	...	...	...	...	...	27·0	49·1	45·5	...	...
Calcium .	22·5	1·6	...	...	...	...	23·4	...	...	...	...	...
Strontium	...	0	...	...	...	...	...	...	39·2	26·5	...	...
Barium .	...	9·8	...	...	...	...	23·9	...	39·8	27·0	...	...
Magnesium	22·1	2·0	...	...	...	...	22·5	0	...	18·8	...	...
Zinc . .	...	...	...	...	...	...	21·85	0	...	...	...	...
Iron . .	...	...	...	...	...	...	24·0	0	...	...	...	...
Cobalt .	22·1	...	...	...	...	...	22·0	...	...	...	...	...
Copper .	22·0	8·1	...	...	...	...	22·0	0	...	18·2	...	...
Lead . .	24·5	...	...	...	...	...	24·1	...	38·4	25·4	...	...
Mercury .	22·0	18·4	...	...	...	...	...	...	...	...	...	...
Silver . .	25·9	...	...	...	...	...	29·4	...	39·2	27·2	...	...

(1522) 4. *Atomic Volumes of Liquids of Analogous Composition.*—In the year 1842 an important paper was published by Kopp (Liebig's *Annal.* xli. 79, 169), in which he showed that when liquids belonging to one homologous series are compared with corresponding terms of other collateral homologous series (*vide* Table, p. 34), like differences are observed in their atomic volumes. When, for instance, the atomic volume of a hydrated acid (HO,A) (A representing an equivalent of any monobasic anhydrous acid) is compared with its corresponding vinic ether (C_4H_5O,A), the atomic volume of the hydrated acid, at ordinary temperatures, is about 534 less than that of the corresponding compound ether. The atomic volume of the hydrated acid (HO,A) is about 300 less than that of its corresponding methylic compound (C_2H_3O,A); and as a necessary consequence, the atomic volume of an ethylic compound is about 234 greater than that of the corresponding methylic compound. A more careful examination of the subject has shown that the somewhat considerable divergences observed between the atomic volumes calculated according to these laws, and those actually found by observation, are materially reduced if the liquids be compared, not at *equal* temperatures, but at *corresponding* temperatures. Corresponding temperatures are those at which the cohesion of the liquids compared is equal; or temperatures at which the liquids emit vapours of equal tension. The tension of the vapours of different liquids through the required range of the thermometric scale is, however, only known in a few instances; but it may be assumed without any very serious error, that corresponding temperatures in liquids are those situated at equal distances below the boiling points of the liquids under comparison. Thus, if the boiling point of alcohol be 173°, and if that of ether be 94°, the temperature of 60° F. would not be a corresponding temperature for these liquids; but if the alcohol be at 60°, which is 113° below its boiling point, the corresponding temperature for ether would be 113° below its boiling point, or $-19°$.

The atomic volume v of a compound increases as the temperature rises. This, indeed, must be evident from the consideration that the specific gravity d diminishes as the temperature rises, whilst the equivalent number or molecular weight q remains constant; and since $\frac{q}{d} = v$, the atomic volume must necessarily vary inversely as the density of the body, and consequently must increase as the temperature rises. In making comparisons of atomic volumes of compounds it is found advantageous in practice always to calculate them for the boiling point of the respective liquids under a pressure equal to that of 30 inches of mercury.

At the time when Kopp first called attention to the atomic volume of liquids, few really exact data existed, by means of which his conclusions could be rigidly tested. Since that period both Pierre (*Ann. de Chimie*, III. xv. 325; xix. 193, and xx. 5,) and Kopp himself (*Poggendorff's Annal.* lxxii. 1 and 223, *Liebig's Annal.* xciv. 257, xcv. 307), have published a series of important and elaborate researches upon the specific gravity, the expansion, and the boiling points of a considerable number of liquids, by means of which the atomic volume of these liquids at the boiling point may be calculated. The following Table contains the results of Kopp's inquiries arranged for the convenience of comparison:—

[illegible] acid . . .	$HO,C_{14}H_5O_3$	1525	1·0838†
[illegible] anhydride .	$C_4H_3O_3,C_4H_3O_3$	1275	1·0969
[illegible]	$C_8H_{10}O_2$	925	0·7366
[illegible] of methyl	C_2H_3O,C_2HO_3	750	0·9984
[illegible] of methyl }	$C_2H_3O,C_4H_3O_3$	925	0·9562
[illegible] of ethyl }	C_4H_5O,C_2HO_3	925	0·9394
[illegible] of ethyl .	$C_4H_5O,C_4H_3O_3$	1100	0·9105
Butyrate of methyl }	$C_2H_3O,C_8H_7O_3$	1275	0·9210
Propionate of ethyl }	$C_4H_5O,C_6H_5O_3$	1275	0·9231
Valerate of methyl }	$C_2H_3O,C_{10}H_9O_3$	1450	0·9015
Butyrate of ethyl }	$C_4H_5O,C_8H_7O_3$	1450	0·9041
Acetate of tetryl }	$C_8H_9O,C_4H_3O_3$	1450	0·9004
Formiate of amyl }	$C_{10}H_{11}O,C_2HO_3$	1450	0·8945
Valerate of ethyl }	$C_4H_5O,C_{10}H_9O_3$	1625	0·8829
Acetate of amyl }	$C_{10}H_{11}O,C_4H_3O_3$	1625	0·8837
Valerate of amyl .	$C_{10}H_{11}O,C_{10}H_9O_3$	2150	0·8793
Benzoate of methyl	$C_2H_3O,C_{14}H_5O_3$	1700	1·1026
Benzoate of ethyl .	$C_4H_5O,C_{14}H_5O_3$	1875	1·0657
Benzoate of amyl .	$C_{10}H_{11}O,C_{14}H_5O_3$	2400	1·0039
Cinnamate of ethyl	$C_4H_5O,C_{18}H_7O_3$	2200	1·0656
Salicylate of methyl	$C_2H_3O,C_{14}H_5O_5$	1900	1·1969
Carbonate of ethyl .	$C_5H_{10}O_2,C_2O_4$	1475	0·9998
Oxalate of methyl .	$C_4H_6O_2,C_4O_6$	1475	1·1566‡
Oxalate of ethyl .	$C_8H_{10}O_2,C_4O_6$	1825	1·1016
Succinate of ethyl .	$C_8H_{10}O_2,C_8H_4O_6$	2175	1·0718
Acetone	$C_6H_6O_2$	725	0·8144
Aldehyd	$C_4H_4O_2$	550	0·8009
Valeraldehyd . .	$C_{10}H_{10}O_2$	1075	0·8224
Hydride of benzoyl	$C_{14}H_6O_2$	1325	1·0636
Hydride of cumyl .	$C_{20}H_{12}O_2$	1850	0·9832
[illegible]	$C_{12}H_6$	975	0·8991
[illegible]	$C_{20}H_{14}$	1675	0·8778
Naphthalin . . .	$C_{20}H_8$	1600	0·9774§
[illegible]	$C_{16}H_{18}$	1425	0·7135

(1523) *Discussion of Kopp's Conclusions.*—The atomic volumes iven in the foregoing table are those calculated by Kopp for the *oiling point* of their respective liquids given in the fifth column f the table. These boiling points are not in all cases the actual umbers obtained by experiment, but are in some instances modiied according to considerations explained in (1524), since the oiling point of many substances is only approximatively known, he estimates of different observers sometimes varying several egrees. The atomic volumes contained in this table, therefore, iffer from the earlier calculations already referred to, which were ll made at ordinary temperatures. Now if we compare the hyrated acids contained in Division II. of the table with the ethers n Division III., it appears that the atomic volume of the hydrated cid is about 540 less than that of the corresponding ether; for nstance:—

	At. vol.		At. vol.		At. vol.
utyric ether =	1867·0	Acetic ether =	1347·5	Formic ether =	1071·2
utyric acid =	1347·5	Acetic acid =	797·5	Formic acid =	522·5
Difference	519·5		550·0		548·7

he difference between the atomic volume of the hydrated acid nd that of its corresponding methylic compound is about 260:—

utyr. methyl =	1581·2	Acet. methyl =	1072·5	Form. methyl =	792·5
utyric acid =	1347·5	Acetic acid =	797·5	Formic acid =	522·5
	233·7		275·0		270·0

nd, as may be seen by inspection of the table, the mean difference etween the atomic volume of the corresponding compounds in the hyl and the methyl series is about 287:—

aler. ethyl =	2170·0	Butyr. ethyl =	1867·0	Acet. ethyl =	1347·5
aler. methyl =	1870·0	Butyr. methyl =	1581·2	Acet. methyl =	1072·5
	300·0		285·8		275·0

Now, since the corresponding compounds of the ethylic and the ethylic series differ by (C_2H_2), this mean difference in the atomic lume of such corresponding compounds has been assumed by opp to represent the volume occupied by each equivalent of (C_2H_2) hen in combination. This difference, it will be seen from the regoing table, ranges in a large number of compounds between 50 and 300. Kopp fixes 275 as its average value at the boiling int of each compound.

Isomeric liquids of analogous composition, such, for instance, the different metameric compound ethers, possess atomic lumes which are sensibly equal to each other, and they conseuently *at their boiling points* have the same specific gravities; uch, for instance, as:—

Butyric acid	$HO,C_8H_7O_3=1347{\cdot}5$	Valer. methyl	$C_2H_3O.C_{10}H_9O_3=1870$
Acetic ether	$C_4H_5O,C_4H_3O_3=1347{\cdot}5$	Butyr. ethyl	$C_4H_5O,C_8H_7O_3=1867$

Numerous other cases may also be seen by comparing the volumes of the ethers which are bracketed together in the table, p. 880. But if the isomeric compounds belong to different and dissimilar series having a dissimilar typical constitution, the same correspondence is not observed; for example:—

Acetone . . .	$(C_6H_6O_2)_2=1960{\cdot}0$	Aldehyd . . .	$(C_4H_4O_2)_2=1422{\cdot}4$
Valerate of methyl	$C_2H_3O,C_{10}H_9O_3=1870{\cdot}0$	Butyric acid	$HO,C_8H_7O_3=1347{\cdot}5$
	$90{\cdot}0$		$74{\cdot}9$

By comparing together liquids which contain the same number of elementary atoms, but in which a certain number of atoms of oxygen have been substituted for a similar number of equivalents of hydrogen, it is found that the atomic volume of oxygen is somewhat greater than that of hydrogen; as for example:—

Acetic anhydride	$C_8H_6O_6=1376{\cdot}0$	Acetic acid	$C_4H_4O_4=797{\cdot}5$
Butyric acid . .	$C_8H_8O_4=1347{\cdot}5$	Alcohol	$C_4H_6O_2=781{\cdot}0$
	$28{\cdot}5$		$16{\cdot}5$

From a similar comparison of compounds in which a certain number of atoms of carbon have taken the place of an equal number of equivalents of hydrogen, it has been concluded that the volumes of carbon and of hydrogen are equal. This is exemplified, according to Kopp, in the corresponding compounds of the valeric ($C_{10}H_{10}O_4$), and the benzoic ($C_{14}H_6O_4$) acids; but the examples which he has selected to prove this point indicate that there is a slight difference in the volumes of the two elements; thus:—

Benzoate of methyl	= 1879	Benzoic ether	= 2185	Benzoate of amyl	= 3096
Valerate of methyl	= 1870	Valeric ether	= 2170	Valerate of amyl	= 3051
	9		15		45

This difference, however, is so slight, that in computing atomic volumes from the composition of a body, each atom of carbon and hydrogen may be considered to occupy equal volumes. Kopp concludes that the atom of each element, in entering into combination, does so with its own specific volume; and he further assumes that the same element may have *different* specific volumes according to the position which it occupies in the compound. Oxygen, for example, has a value when it forms a part of the radicle, different from that which it possesses when external to the radicle:—Thus, if O=100 and H=12·5 at the boiling point of the different compounds,

The volume of an atom of carbon . . . . = 68·75
" " of hydrogen . . . . = 68·75
" " of oxygen within the radicle . = 76·75
" " " external to the radicle = 48·75
Sulphur within the radicle . . . . = 178·75
" external to the radicle . . . . = 142·75
Chlorine " . . . . = 285·00
Bromine " . . . . = 347·50
Iodine " . . . . = 468·75

Kopp, by the employment of these numbers for each atom of the above-mentioned elements present in the molecule of any compound, has arrived by calculation, in a large number of cases, at a close approximation to the observed atomic volume. For example:—Calculating the atomic volumes of alcohol $\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2$ and of acetic acid $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$ from the numbers given above, the results would be as follows:—

For alcohol.	For acetic acid.
$C_4 = 68·75 \times 4 = 275$	$C_4 = 68·75 \times 4 = 275$
$H_6 = 68·75 \times 6 = 412·5$	$H_4 = 68·75 \times 4 = 275$
$O_2 = 48·75 \times 2 = 97·5$	$O_2 = 76·75 \times 2 = 153·5$
	$O_2 = 48·75 \times 2 = 97·5$
Calculated 785·0	Calculated 801·0
Observed 781	Observed 797·5

It sometimes happens that equal volumes of two different liquids will contain an equal number of molecules of their constituent compounds; but this, which is the rule with bodies in the condition of gas or vapour, is the exception in the case of liquids.

For the further prosecution of this subject the reader is referred to Kopp's interesting papers in Liebig's *Annalen*, Bd. xcv., xcvi., xcvii., and xcviii.

(1524) *Kopp's Law of the Boiling Points.*—At the same time that Kopp pointed out the regular increase in atomic volume which the successive terms of the same homologous series exhibit, he called attention to a not less remarkable regularity in the increase of the temperature required to produce ebullition as the number of equivalents of (C_2H_2) increases in the compound. By inspecting the table at p. 880, Div. III., it will be seen, on comparing the boiling points of the compounds of ethyl and of methyl, that for every addition of C_2H_2 in the empirical formula, a rise in the boiling point of about 36° F. takes place.

It may be stated as a general result of observation, that the boiling point of a hydrated acid is 113°·4 higher than that of its methylic ether, 79°·2 higher than that of its ethylic ether, and

23°·4 lower than that of its amylic ether: the boiling point of an alcohol of the form $C_{2n}H_{2n+2}O_2$ is about 72° lower than that of its corresponding acid $C_{2n}H_{2n}O_4$, a compound ether of the form $(C_{2n}H_{2n+1}O,C_{2n}H_{2n-1}O_3)$ boils at about 147°·6 below the acid $(C_{2n}H_{2n}O_4)$ which is isomeric with it.

The rise of temperature for each additional equivalent of C_2H_2 differs, however, in different classes of homologous compounds, as may be seen by an examination of the following table, from which it appears that in the *alcohols* the mean elevation of the boiling point for C_2H_2 is 31°·4. In the *aldehyds* it is 47°, though in this class the divergences from the mean are so considerable that it is probable that several of the assigned boiling points are inaccurate. In the *radicles of the alcohols* the mean rise is 42°, and in the *homologues of benzol* it is 41°. In the *acids* of the acetic series it is 38°·9, and in the aniline *bases* it is 30°·5.

Ethers.	Formula.	Observed Boiling Point.
Methylic ether . .	$C_4H_6O_2$	−5°·8, Berthelot.
Methylethylic ether	$C_6H_8O_2$	+51°·8, Williamson.
Ethylic ether . .	$C_8H_{10}O_2$	93°·2, Dumas; 93°·5, Kopp; 94°·8, Andrews; 95°, Delffs; 95°·9, Pierre; 96°·3, Gay-Lussac.
Methyl amylic ether	$C_{12}H_{14}O_2$	161°·6, Williamson.
Ethyl tetrylic ether	$C_{12}H_{14}O_2$	172°·4—176°, Wurtz.
Ethyl amylic ether	$C_{14}H_{16}O_2$	233°·6, Williamson.
Tetrylic ether . .	$C_{16}H_{18}O_2$	212°—219°·2? Wurtz.
Amylic ether . .	$C_{20}H_{22}O_2$	338°·0, Gaultier; 338°—347°, Wurtz; 347° to 361°, Rieckher.
Mean difference for $C_2H_2 = 44°$ F.		
Alcohols.		
Wood spirit . . .	$C_2H_4O_2$	148°—149°·2, Kopp; 140°, Kane; 140°·9—141°·8, Delffs.
Ethylic alcohol . .	$C_4H_6O_2$	172°·4—173°·8, Kopp; 172°·2, Andrews; 173°, Pierre; 173°·1, Gay-Lussac.
Tritylic do. . . .	$C_6H_8O_2$	204°·8, Chancel.
Tetrylic do. . . .	$C_8H_{10}O_2$	228°·2, Wurtz.
Amylic do. . . .	$C_{10}H_{12}O_2$	266°·7—271°·4, Kopp; 269°·4, Pierre; 269°·6, Delffs, Cahours.
Hexylic do. . . .	$C_{12}H_{14}O_2$	298°—309°, Faget.
Heptylic do. . . .	$C_{14}H_{16}O_2$	350°·6—351°·5, Stœdeler.
Octylic do. . . .	$C_{16}H_{18}O_2$	360°, Bouis; 352°·4, Moschnin.
Mean difference for $C_2H_2 = 31{\cdot}4$ F.		
Aldehyds.		
Acetic	$C_4H_4O_2$	71°·4, Liebig; 71°·6, Pierre; 67°·8, Kopp.
Propionic	$C_6H_6O_2$	131°—149°, Guckelberger.
Butyric	$C_8H_8O_2$	154°—167°, Guckelberger.
Valeric	$C_{10}H_{10}O_2$	199°·2, Kopp; 204°·8—206°·6, Parkinson; 206°·6, Limpricht.
Œnanthylic . . .	$C_{14}H_{14}O_2$	311°—316°·4, Bussy.
Caprylic	$C_{16}H_{16}O_2$	?
Capric	$C_{20}H_{20}O_2$	446°, Gerhardt.
Mean difference for $C_2H_2 = 47°$ F.		

Acids.	Formula.	Observed Boiling Point.
o.	$C_2H_2O_4$	209°·3, Liebig ; 212°, Wurtz ; 221°·7, Kopp.
. . . . . .	$C_4H_4O_4$	240°·8, Delffs ; 242°·4, Kopp.
nic	$C_6H_6O_4$	286°·9, Kopp ; about 284°, Dumas and others.
c	$C_8H_8O_4$	312°·8, Kopp, Delffs ; 325°·4, Pierre ; 327°·2, Pelouze.
c	$C_{10}H_{10}O_4$	346°·1, Delffs ; 347°, Dumas and Stas ; 348°·4, Kopp.
c	$C_{12}H_{12}O_4$	388°·4, Brazier and Gossleth ; 395°·6—408°, Fehling.
thylic . . .	$C_{14}H_{14}O_4$	424°·4, Stœdeler.
ic	$C_{16}H_{16}O_4$	456°·8, Fehling.
onic . . .	$C_{18}H_{18}O_4$	500°·0, Cahours.

Mean difference for $C_2H_2 = 36°$.

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hydrides.

. . . . . .	$C_8H_6O_6$	280°·4, Gerhardt, Kopp ; 278°·6, Wurtz.
nic	$C_{12}H_{10}O_6$	336°·2, Limpricht and Uslar.
c	$C_{16}H_{14}O_6$	About 374°, Gerhardt.
. . . . .	$C_{20}H_{18}O_6$	About 419°, Gerhardt.
ic	$C_{32}H_{30}O_6$	About 554°, Chiozza.

Mean difference for $C_2H_2 = 22°·7$.

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hylic Ethers.

ate of methyl	$C_2H_3O,C_2H\ O_3$	90°·8, Kopp ; 91°·2, Andrews.
e	$C_2H_3O,C_4H_3O_3$	131°, Andrews ; 132°·3—132°·6, Kopp ; 139°·1, Pierre.
nate . . .	$C_2H_3O,C_6H_5O_3$	?
ate	$C_2H_3O,C_8H_7O_3$	199°·4, Delffs ; 203°—203°·2, Kopp ; 215°·8, Pierre.
te	$C_2H_3O,C_{10}H_9O_3$	237°·2—240°·0, Kopp.

Mean difference for $C_2H_2 = 37°·2$.

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ylic Ethers.

ate of ethyl .	$C_4H_5O,C_2H\ O_3$	127°·2, Pierre ; 127°·4, Delffs ; 128°, Liebig ; 130°·5—131°·5, Kopp.
e	$C_4H_5O,C_4H_3O_3$	164°·7, Kopp ; 165°·2, Dumas, Delffs, Pierre.
nate . . .	$C_4H_5O,C_6H_5O_3$	204°·5—208·4, Kopp ; 213°·8, Limpricht and Uslar.
ate	$C_4H_5O,C_8H_7O_3$	230°, Lerch ; 235°·4, Delffs ; 237°·7, Kopp ; 246°·2, Pierre.
te	$C_4H_5O,C_{10}H_9O_3$	268°·7, Delffs ; 271°·8, Kopp ; 272°·3, Otto ; 271°·4—273°·2, Berthelot.
ate	$C_4H_5O,C_{12}H_{11}O_3$	248°? Lerch ; 323°·6, Fehling.
onate . . .	$C_4H_5O,C_{18}H_{17}O_3$	420°·8—424°·4, Cahours ; 435°·2, Delffs.

Mean difference for $C_2H_2 = 38°·8$.

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her Ethers.

e of trityl .	$C_6H_7O,C_4H_3O_3$	2 × 36	About 194°, Berthelot.
ate of trityl .	$C_6H_7O,C_8H_7O_3$		About 266°, do.
ate of tetryl .	$C_8H_9O,C_2H\ O_3$	25·2	About 212°, Wurtz.
e of tetryl .	$C_8H_9O,C_4H_3O_3$		237°·2, do.

Compound Ethers.	Formula.	Observed Boiling Point.
Formiate of amyl .	$C_{10}H_{11}O,C_2\ H\ O_3$	237° 2, Delffs ; about 240°·8, Kopp.
Acetate	$C_{10}H_{11}O,C_4\ H_3\ O_3$	271°·4, Delffs ; 272°—279°·1, Kopp.
Propionate . . .	$C_{10}H_{11}O,C_6\ H_5\ O_3$	About 311°, Wrightson.
Valerate	$C_{10}H_{11}O,C_{10}H_9\ O_3$	372°—372°·9, Kopp.
Caproate	$C_{10}H_{11}O,C_{12}H_{11}O_3$	411°·8, Brazier and Gossleth.
	Mean difference for $C_2H_2 = 34°·9$.	
Acetate of octyl .	$C_{16}H_{17}O,C_4\ H_3\ O_3$	379°·4, Bouis,
Laurate of ethyl .	$C_4\ H_5\ O,C_{24}H_{23}O_3$	507°, Georgey ; 516°, Delffs.
Alcohol Radicles.		
Ethyl tetryl . . .	$C_{12}H_{14}$	143°·6, Wurtz.
Trityl	$C_{12}H_{14}$	154°·4, Williams.
Methyl hexyl . .	$C_{14}H_{16}$	179°·6, Wurtz.
Ethyl amyl . . .	$C_{14}H_{16}$	190°·4, do.
Tetryl	$C_{16}H_{18}$	222°·8, Wurtz ; 226°·4, Kolbe ; 227°·3, Kopp.
Tetryl amyl . . .	$C_{18}H_{20}$	269°·6, Wurtz.
Amyl	$C_{20}H_{22}$	311°, Frankland ; 316°·4, Wurtz.
Tetryl hexyl . . .	$C_{20}H_{22}$	311°, Wurtz.
Hexyl	$C_{24}H_{26}$	395°·6, Brazier and Gossleth, Williams.
	Mean difference for $C_2H_2 = 42°$.	
Hydrocarbons.		
Benzol	$C_{12}H_6$	176°·7, Kopp ; 176°·9, Mansfield ; 177°·6, Church.
Toluol	$C_{14}H_8$	218°7, Church ; 222°·8, Glenard and Boudault ; 226°·4, Deville, Pelletier and Walter ; 229°·1, Noad ; 235°·4, Mansfield.
Xylol	$C_{16}H_{10}$	259°·1, Church ; 264°·2, Cahours.
Cumol	$C_{18}H_{12}$	298°·4, Abel ; 299°·1, Church ; 304°·5, Gerhardt.
Cymol	$C_{20}H_{14}$	339°·2, Church ; 339°·8, Mansfield ; 340°·7, Noad ; 351°·5, Kopp.
	Mean difference for $C_2H_2 = 41°$.	

In the homologous ethers, which contain chlorine, bromine, iodine, and sulphur, the difference in the boiling point produced by each successive addition of C_2H_2 is considerably higher than in the compound ethers. For example :—

Compounds.	Formula.	Difference.	Observed Boiling Point.
Chloride of methyl .	$C_2\ H_3\ Cl$		— 4°, Berthelot.
Chloride of ethyl .	$C_4\ H_5\ Cl$	55°·8	+ 51°·8, Pierre.
Chloride of tetryl .	$C_8\ H_9\ Cl$	2 × 52°·5	158°—167°, Wurtz.
Chloride of amyl .	$C_{10}H_{11}Cl$	48	215°·6, Pierre, Cahours.
Chloride of octyl .	$C_{16}H_{17}Cl$	43	347°, Bouis.
	Mean difference for $C_2H_2 = 50°$.		
Bromide of methyl	$C_2\ H_3\ Br$		55°·4, Pierre.
Bromide of ethyl .	$C_4\ H_5\ Br$	50	105°·8, do.
Bromide of tetryl .	$C_8\ H_9\ Br$	2 × 43°·2	192°·2, Wurtz.
Bromide of amyl .	$C_{10}H_{11}Br$	54	246°·2, Pierre.
Bromide of octyl .	$C_{16}H_{17}Br$	43	374°, Bouis.
	Mean difference for $C_2H_2 = 45°·5$.		

mpounds.	Formula.	Difference.	Observed Boiling Point.
of methyl .	C_2H_3I		107°·6, Andrews; 111°·2, Pierre.
of ethyl . .	C_4H_5I		158°·0, Pierre; 159°·8, Andrews; 161°·6, Frankland.
of tetryl . .	C_8H_9I		249°·8, Wurtz.
of amyl . .	$C_{10}H_{11}I$		294°·8, Frankland; 298°·4, Kopp; 300°, Grimm.
of octyl . .	$C_{16}H_{17}I$		410°, Bouis.
Mean difference for $C_2H_2 = 43°$.			
e of methyl	$C_4H_6S_2$		105°·8, Regnault.
e of ethyl .	$C_8H_{10}S_2$	2 × 45	195°·8, Pierre.
e of amyl .	$C_{20}H_{22}S_2$	6 × 37	420°·8, Balard.
Mean difference for $C_2H_2 = 40°$.			
mercaptan .	C_2H_3S,HS		69°·8? Gregory.
ercaptan .	C_4H_5S,HS	27?	96°·8, Liebig.
nercaptan .	C_8H_9S,HS	2 × 46°·8	190°·4, Humann.
ercaptan .	$C_{10}H_{11}S,HS$	57°·6	242°·6, Krutsch; 248°, Kopp.
Mean difference for $C_2H_2 = 50°$.			

Bases.	Formula.	Observed Boiling Point.
. . . . .	$C_{12}H_7N$	359°·6, Hofmann.
a	$C_{14}H_9N$	388°·4, Muspratt and Hofmann.
. . . . .	$C_{16}H_{11}N$	415°·4—417°·2, Church.
lia. . . .	$C_{18}H_{13}N$	437°, Nicholson.
lia. . . .	$C_{20}H_{15}N$	482°, Barlow.
Mean difference for $C_2H_2 = 30°·6$.		
e	$C_{10}H_5N$	240°, Anderson.
. . . . .	$C_{12}H_7N$	271°·4, do.
e	$C_{14}H_9N$	310°, do.
e	$C_{16}H_{11}N$	356°, do.
Mean difference for $C_2H_2 = 38°·7$.		

e following series exhibits a curious departure from the egularity exhibited by homologous compounds:—

Nitriles.	Formula.	Observed Boiling Point.
of methyl .	C_2H_3,C_2N	Kopp, 161°·6; Dumas, 170°·6; Hofmann and Buckton, 170°·6—172°·4.
of ethyl .	C_4H_5,C_2N	Kolbe, Meyer, 190°·4; Grimm, 208°·4.
of trityl .	C_6H_7,C_2N	Dumas and others, 245°.
of tetryl .	C_8H_9,C_2N	Schlieper, 257°; Guckelberger, 257°—262°
of amyl .	$C_{10}H_{11},C_2N$	Frankland and Kolbe, 294°·8; Wurtz, 311°

onsiderable irregularities are also observed in the boiling of many of the derivatives of the diatomic alcohols; for example, in the alcohols themselves, as the proportion of multiples of C_2H_2 increases the boiling point falls.

Glycol Derivatives.	Formula.	Observed Boiling Point.
Glycol	$C_4H_6O_4$	383°, Wurtz.
Trityl glycol . . .	$C_6H_8O_4$	370°—372° do.
Tetryl glycol . .	$C_8H_{10}O_4$	361°·4—363° do.
Amyl glycol . . .	$C_{10}H_{12}O_4$	350°·6 do.
Mean difference for $C_2H_2 = 11°·2$.		
Bichloride of ethylene	$C_4H_4Cl_2$	185°—186°·8, Dumas; 185°, Pierre.
Bichloride of tritylene	$C_6H_6Cl_2$	212°—217°·4, Reynolds; 219°·2, Cahours.
Bichloride of tetrylene	$C_8H_8Cl_2$	251°·6, Kopp; 253°·4, Kolbe.
Bichloride of amylene	$C_{14}H_{14}Cl_2$	368°·6, Limpricht.
Bibromide of ethylene	$C_4H_4Br_2$	266°.
Bibromide of propylene	$C_6H_6Br_2$	293°.
Bibromide of amylene	$C_{10}H_{10}Br_2$	320°.
Mean difference for $C_2H_2 = 27°$.		

The ethers of acids homologous with oxalic acid, $C_{2n}H_{2n-4}O_8$ are isomeric with certain ethers of the diatomic alcohols, which affords an opportunity of contrasting these bodies; but it must be admitted that the accuracy of the numbers given for some of the glycolic ethers is questionable.

Compound Ethers.	Formula.	Observed Boiling Point.
Oxalate of methyl . .	$C_8H_6O_8$	321°·8, Dumas and Péligot; 327°·2, Delffs.
Oxalate of ethyl . . .	$C_{12}H_{10}O_8$	365°, Kopp; 366°·8, Delffs.
Succinate of methyl . .		388°·4, Fehling.
Binacetate of glycol . .		366°·8—368°·6, Wurtz.
Binacetate of tritylglyco	$C_{14}H_{12}O_8$	366°·8, Wurtz.
Succinate of ethyl . .	$C_{16}H_{14}O_8$	417°·2, D'Arcet, Fehling; 422°·6, Kopp;
Binacetate of tetrylglycol		about 392°, Wurtz.
Butyro-acetate of glycol		406°—419°, Simpson.
Binacetate of amylglycol	$C_{18}H_{16}O_8$	above 392°, Wurtz.
Butyro-acetate of glycol		about 446°, Lourenço.
Bibutyrate of glycol .	$C_{20}H_{18}O_8$	462°—466°, Wurtz.
Suberate of ethyl . .	$C_{24}H_{22}O_8$	500°, Laurent.
Oxalate of amyl . . .		500°, Cahours; 503°·6, Balard.
Sebate of methyl . .		545°, Carlet.
Bivalerate of glycol . .		about 491°, Lourenço.
Sebate of ethyl . . .	$C_{28}H_{26}O_8$	586°, Carlet.

A comparison of metameric bodies of analogous composition shows that the boiling points of such compounds coincide very nearly, whereas if they belong to series which differ in their composition, the boiling points may vary widely. The differences between the hydrated acids and the compound ethers metameric with them, given in the table p. 885, show the latter point very clearly.

Many of the differences observed between the boiling points obtained by experiment, and the theoretical numbers, (calculated according to Kopp's law of a constant difference,) may possibly disappear when the boiling points shall have been more accurately determined: but Kopp observes, that it must not be assumed that the boiling points of liquids, when compared at *any* given pressure, will always exhibit the same differences as they do when compared at the average pressure of 30 inches of mercury. It does not follow, for instance, though the boiling point of ether is 79°·5 below that of alcohol, under a pressure of 30 inches, that under a pressure of 15 inches, the difference between these boiling points should still be 79°·5: since it is well known that what is called Dalton's law (177), viz., that 'all liquids at equal distances from their boiling point, emit vapours of equal tension,' is not correct.

The accurate determination of the boiling point of a liquid is by no means easy, as might be inferred from an inspection of the foregoing tables, where many experimentalists of great skill and experience give for the same well-known substances, numbers which differ by several degrees from each other. Indeed, it has been found, independently of the irregular manner in which many liquids boil in glass vessels (167), that in several cases impurities so slight as not materially to affect the result of ultimate analysis of the substance, may yet produce a considerable effect upon its boiling point.

Numerous attempts have been made to determine the effect which the addition or the removal of a certain number of equivalents of each of the elements, carbon, hydrogen, and oxygen, exerts upon the boiling point of the resulting compound. These attempts, however, have not led to any satisfactory result, since the compounds thus compared belong generally to different series. The aldehyds, for example, cannot satisfactorily be compared with the alcohols, and it is only in the same homologous series that an equal rise in the boiling point can be expected for equal increments in the number of the constituent elements.

In the case of the alcohols, the volatile acids, and the compound ethers,—Kopp, assuming a constant difference of 34°·2 F. for C_2H_2, has calculated a table of boiling points which approximate pretty closely to the observed numbers, the mean of the best observations of which are contrasted with Kopp's calculated numbers.

If the calculated results given in the ensuing table be assumed to be accurate, it follows, if one of the bodies contained in this table be compared with others analogous to it in composition, that the boiling point will be raised by about 26°·1 for each additional equivalent of carbon; and that it will be reduced by about 26°·1, for a diminution of each equivalent of carbon: but the effect produced by hydrogen is the reverse of that produced by carbon; since for every additional equivalent of hydrogen, the boiling point is lowered 9°; and for every equivalent of hydrogen which is removed, it is raised 9°:—

Alcohols.			Acids.			Compound Ethers.		
$C_{2n}H_{2n+1}O, + HO.$	Observed.	Calculated.	$HO + C_{2n}H_{2n-1}O_3$	Observed.	Calculated.	$C_{2n}H_{2n+1}O + C_{2n}H_{2n-1}O_3.$	Observed.	Calculated.
$C_2H_4O_2$	140°·5	138°·2	$C_2H_2O_4$	210°·6	210°·2			
$C_4H_6O_2$	173°·0	172°·4	$C_4H_4O_4$	241°·6	244°·4	$C_4H_4O_4$	91°·0	96°·8
$C_6H_8O_2$	204°·8	206°·6	$C_6H_6O_4$	285°·5	278°·6	$C_6H_6O_4$	131°·8	131°·0
$C_8H_{10}O_2$	228°·2?	240°·8	$C_8H_8O_4$	312°·8	312°·8	$C_8H_8O_4$	165°·0	165°·2
$C_{10}H_{12}O_2$	269°·5	275°·0	$C_{10}H_{10}O_4$	347°·2	347°·0	$C_{10}H_{10}O_4$	201°·3	199°·4
$C_{12}H_{14}O_2$	309°·0	309°·2	$C_{12}H_{12}O_4$	388°·4	381°·2	$C_{12}H_{12}O_4$	236°·5	233°·6
$C_{14}H_{16}O_2$	?	343°·4	$C_{14}H_{14}O_4$	?	415°·4	$C_{14}H_{14}O_4$	270°·9	267°·8
$C_{16}H_{18}O_2$	360°·0	377°·6	$C_{16}H_{16}O_4$	456°·8	449°·6	$C_{16}H_{16}O_4$	311°·?	302°·0

The following compounds are adduced by Kopp as affording an illustration of this alteration of the boiling point by the addition of carbon and hydrogen, in isologous compounds; but the experimental numbers often differ very considerabl y from the calculated values:—

Alcohols (C$_{2n}$H$_{2p}$O$_2$).		Calculated.	Observed Boiling Point.
Allylic	$C_6H_6O_2$	224°·6	217°·4, Hofmann & Cahours.
Phenylic.	$C_{12}H_6O_2$	381°·2	368°·6 — 370°·4. Laurent; 370°·4, Kopp.
Benzoic . . . . . . :	$C_{14}H_8O_2$	415°·4	399°·2, Cannizzaro; 404°·6, Kopp.
Cinnamic	$C_{18}H_{10}O_2$	501°·8	482°, Wolff; 489°·2, E. Kopp.
Cuminic	$C_{20}H_{14}O_2$	518°·0	469°·4, Kraut.

Compound Ethers, $C_{2n}H_{2p}O_4$.		Calculated.	Observed Boiling Point.
Acetate of allyl . . .	$C_{10}H_8O_4$	217°·4	208°·4—212°, Hofmann and Cahours; 221°, Zinin.
Butyrate of allyl . . .	$C_{14}H_{12}O_4$	285°·8	284°, Hofmann and Cahours; about 293°, Berthelot.
Valerate of allyl . . .	$C_{16}H_{14}O_4$	320°·0	323°·6, Hofmann & Cahours.
Acetate of phenyl . . } Benzoate of methyl . . }	$C_{16}H_8O_4$	374°·0	370°·4, Scrugham. 390°·2, Dumas and Peligot, Kopp.
Benzoate of ethyl . . } Acetate of benzyl . . }	$C_{18}H_{10}O_4$	408°·2	404°·6, Delffs; 408°·2, Dumas; 415°·4, Kopp. 410°, Cannizzaro.

[*Continued.*]

Compound Ethers, $C_{2n}H_{2p}O_4$.		Calculated.	Observed Boiling Point.
Toluate of ethyl . . .	$C_{20}H_{12}O_4$	442°·4	442°·4, Noad.
Cuminate of ethyl . . Benzoate of amyl . . .	$C_{24}H_{16}O_4$	510°·8	464°, Gerhardt & Cahours. 486° — 489°, Rieckher; 501°·8, Kopp.
Œnanthylate of phenyl	$C_{26}H_{18}O_4$	545°·0	527°—536°, Cahours.
Benzoate of allyl . . . Cinnamate of methyl .	$C_{20}H_{10}O_4$	460°·4	446°, Berthelot and De Luca; 467°·6, Zinin. 465°·8, E. Kopp.
Cinnamate of ethyl . .	$C_{22}H_{12}O_4$	494°·6	500°, Marchand; 503°·6, E. Kopp; 510°·8, H. Kopp.
Benzoate of benzyl . .	$C_{28}H_{12}O_4$	651°·2	653°, Cannizzaro.
Caprylate of phenyl . .	$C_{28}H_{20}O_4$	579°·2	about 572°, Cahours.

The reader will find an admirable digest of this subject by Kopp, in Liebig's *Annalen*, vol. xcvi. and *Phil. Trans.* 1860.

§ II. Atomic Heats.

(1525) *Relation of Specific Heat to Atomic Weights.*—An interesting relation has been traced between the specific heats of bodies and their combining quantities. It has already been stated (161) that the amount of heat required to raise equal weights of different substances 1° in temperature varies for each species of matter, but is always constant for the same body when it is placed under like circumstances. The numbers which represent the respective quantities of heat required to raise each substance through a given number of degrees of the thermometric scale, when referred to that required to raise an equal weight of water through the same interval of temperature, constitute the specific heats of the different bodies.

By comparing together quantities of the various elementary substances in the ratio of their atomic weights, and ascertaining the amount of heat which each requires to raise it through equal intervals of temperature, Dulong and Petit made the important observation that the quantities of heat absorbed bear a very simple numerical relation to each other. In a large proportion of instances, the amounts of heat thus absorbed, allowing for unavoidable errors of experiment, are identical; and it was further observed, that the exceptional cases nearly always exhibit some simple multiple relation to this number. In other words, *the specific heat of an elementary body is inversely as its atomic weight:* consequently, the product of the specific heat of an element into its atomic weight gives, within certain limits for errors of experiment, either a constant number, or some multiple of that number.

The law thus announced by Dulong and Petit has been confirmed by the subsequent researches of Regnault upon specific heat (*Ann. de Chimie,* II. lxxiii. 61, III. i. 129, and ix. 322). Regnault determined the specific heats of a great variety of bodies, both simple and compound. He designates the product obtained by multiplying the specific heat of a body by its atomic weight, as the *atomic heat* of the body.

In 17 of the simple bodies which he examined, most of which were in a state of chemical purity, he found the atomic heat to range between 3·31 and 2·82, with a mean of 3·13. The elements comprised in this class are the following—viz., aluminum, cadmium, cobalt, copper, iron, lead, mercury, nickel, osmium, platinum, rhodium, selenium, sulphur, tellurium, tin, and zinc. A second smaller class was found to have an atomic heat which was double that of the elements contained in the foregoing list. It comprised silver and gold, bismuth, antimony, arsenic and phosphorus, bromine and iodine, as well as potassium and sodium. These bodies gave for their atomic heat, numbers ranging between 5·85 and 6·87, with a mean of 6·42. Regnault has therefore proposed to divide by two, the numbers usually given as the atomic weights of the elements in the second list.

The table which follows includes some of the principal results derived from Regnault's experiments, on a large number of elementary bodies. He found that the same element has a different specific heat if examined in a different state of aggregation: thus planished copper has a smaller specific heat than the same metal after having been annealed. The same fact is exhibited in dimorphous bodies, the densest form having the lowest specific heat: diamond, for example, has a specific heat of 0·1468, whilst graphite has a specific heat one-third higher, or 0·2018; and the specific heat of wood charcoal is still higher, viz., 0·2415. Bodies when in the liquid form have a higher specific heat than when in the solid state, as is seen on comparing the numbers for bromine and mercury in the two conditions.

Specific and Atomic Heats of the Elements.

Elements.	Sp. Heat.	Atomic weight.	Atomic Heat. (Sp. Heat × Eqt.)
Diamond	0·1468	6	0·8808
Graphite	0·2018	"	1·2108
Wood charcoal . .	0·2415	"	1·4490
Sulphur	0·20259	16	3·2414
Selenium	0·0837	39·2	3·3145
Tellurium	0·04737	64	3·031

Specific and Atomic Heats of the Elements.

[*Continued.*]

Elements.	Sp. Heat.	Atomic weight.	Atomic Heat. (Sp. Heat × At. wt.)
Zinc	0·09555	32·5	3·1054
Aluminum	0·2143	13·7	2·9359
Iron	0·11379	28	3·1861
Nickel	0·10863	29·5	3·2045
Cobalt	0·10696	29·5	3·1553
Cadmium	0·05669	55·7	3·1618
Tin	0·05623	58·8	3·2863
Copper	0·09515	31·7	3·0162
Lead	0·03140	103·6	3·2530
Mercury (solid)	0·03192	100	3·192
" (liquid)	0·03332	"	3·332
Platinum	0·03243	98·6	3·1976
Palladium	0·05927	53·2	3·1531
Rhodium	0·05408	52·2	2·8229
Osmium	0·03063	99·4	3·0446
Iridium	0·0363	98·6	3·6
Phosphorus	0·1887	31	5·8497
Iodine	0·05412	127	6·8732
Bromine (solid)	0·0843	80	6·744
" (liquid)	0·106	"	8·48
Potassium	0·6956	39	6·712
Sodium	0·2934	23	6·748
Arsenic	0·08140	75	6·1050
Antimony	0·05077	122	6·1939
Bismuth	0·03084	210	6·4764
Silver	0·05701	108	6·1570
Gold	0·03244	196·6	6·3777

(1526) *Atomic Heats of Compound Bodies.*—The alloys accord-g to Regnault's experiments, yield a specific heat which is xactly the mean of that of their components; hence their atomic eat is equal to the sum of that of their components: but with is exception, the atomic heat of a compound body cannot be alculated from the sum of the atomic heats of its constituents. he atomic heat of the compound is very generally less than at sum, and it varies from this number according as, during ombination, condensation of the component particles has occurred a greater or less extent, and according to other causes hitherto nascertained.

On comparing together equivalent quantities of isomorphous ompounds possessed of a similar chemical composition, Neumann und that they likewise possessed equal atomic heats. The dif-rences from the mean are in some cases considerable, but they re of the same order as those already observed to occur in the imple bodies. The mean atomic heat of the isomorphous carbonates, such, for example, as the carbonates of lime, baryt lead, zinc, strontia, and the double carbonates of lime an nesia, is 21·22, varying between 21·10 and 21·70. In lik ner the sulphates of baryta, lime, strontia, and lead yield atomic heat of 24·82.

Regnault, from an extensive series of experiments, on variety of compound bodies, arrived at the conclusion th all compound bodies of the same atomic composition, similar chemical constitution, the specific heats are inv the atomic weights." The product obtained by multipl specific heat into the atomic weight in any one class of co may, however, differ greatly from the product of the corre numbers in any other class, the numbers furnished by t rent classes not being connected by any very simple ratio. facts will be rendered obvious by an examination of the s summary of Regnault's results (*Ann. de Chimie,* III. i. 1

Atomic Heats.

Class of Bodies.	General Formula.	Atomic Heat. (Sp. Heat × At. wt.)	Nu exa
Elements (1st class)		3·13	
Do. (2nd do.)		6·39	
Protoxides (1st class) (ZnO)	MO	4·99	
Do. (2nd do.) (PbO)	MO	5·76	
Protosulphides	MS	6·20	
Sesquioxides	M_2O_3	13·57	
Sesquisulphides	M_2S_3	15·28	
Binoxides	MO_2	6·92	
Chlorides . 1st class. . (such as BaCl)	MCl	9·36	
Iodides	MI	9·67	
Bromides	MBr	9·68	
Fluorides	MF	8·40	
Chlorides . 2nd class. . (such as NaCl)	MCl	12·84	
Iodides	MI	13·40	
Bromides	MBr	13·70	
Bichlorides	MCl_2	18·64	
Terchlorides	MCl_3	30·22	
Nitrates	MO,NO_5	24·13	
Sulphates . . . 1st class.	$2\,MO,S_2O_6$	26·56	
Carbonates . (2 BaO,C_2O_4)	$2\,MO,C_2O_4$	21·54	
Sulphates . . . 2nd class.	$2\,MO,S_2O_6$	31·08	
Carbonates . (2 NaO,C_2O_4)	$2\,MO,C_2O_4$	29·48	

The specific heat of organic liquids has been only ve fectly studied. In the following table the numbers ethal, and oil of turpentine were determined by Favre a mann. The remaining results are those obtained by Ko

mpound.	Empirical formula.	Molecular weight.	Sp. heat of equal weight.	Sp. heat × mol. weight.
	$(HO)_2$	18	1·000	18·00
irit.	$C_2 H_4 O_2$	32	0·645	20·64
	$C_4 H_6 O_2$	46	0·615	28·29
lcohol.	$C_{10}H_{12}O_2$	88	0·564	49·63
	$C_{32}H_{34}O_2$	242	0·506	122·45
cid.	$C_2 H_2 O_4$	46	0·536	24·65
id.	$C_4 H_4 O_4$	60	0·509	30·54
acid	$C_8 H_8 O_4$	88	0·503	44·26
	$C_8 H_{10}O_2$	74	0·503	37·22
of methyl	$C_6 H_6 O_4$	74	0·507	37·52
ethyl	$C_6 H_6 O_4$	74	0·513	37·96
ethyl	$C_8 H_8 O_4$	88	0·496	49·63
methyl	$C_{10}H_{10}O_4$	102	0·487	49·67
methyl	$C_{12}H_{12}O_4$	116	0·491	56·96
her	$C_{12}H_{10}O_8$	146	0·457	66·72
	$C_6 H_6 O_2$	58	0·530	30·74
	$C_{12}H_6$	78	0·450	35·10
ustard.	$C_8 H_5 NS_2$	99	0·432	42·77
rpentine.	$C_{20}H_{16}$	136	0·467	63·51

these experiments, scanty and few in number though appears that the specific heat of equal weights of com-tances decreases as the molecular weight of the sub-reases; further, that when the products obtained by the specific heat into the molecular numbers are com-product generally increases as the molecular weight and in the homologous series of the alcohols, the fatty the ethers, the increase is about 7 for each addition of e molecule of the compound. In some metameric in the acetate of methyl and formiate of ethyl, the the same, and so is that of ether, which has the same ume as these compounds though it is not metameric

. ATOMIC RELATIONS OF HEAT OF COMBINATION.

The Quantity of Heat developed by Chemical Action is ot only are the specific heats of the elements thus related to each other, but the amount of heat which when entering into combination is definite, and has a lation to the combining number of each substance. same substance is burned with a due supply of oxygen, uitable precautions, a given weight of it always emits mount of heat. Thus 1 lb. of hydrogen, when burned always emits heat enough to melt 315·2 lb. of ice;

31 lb. of phosphorus, when burnt to phosphoric acid, yields heat sufficient to melt 1576 lb. of ice; and 6 lb. of carbon when converted into carbonic acid, emits heat sufficient to melt 350 lb. of ice. It would at first sight appear easy to determine by direct experiment the amount of heat which each body emits in the act of combining with an equivalent of oxygen, and to compare the results thus obtained with a corresponding series of experiments made by combining the same elements with chlorine. Independently, however, of the difficulties which the exact admeasurement of heat always involves, there are others which will be rendered evident by a little consideration.

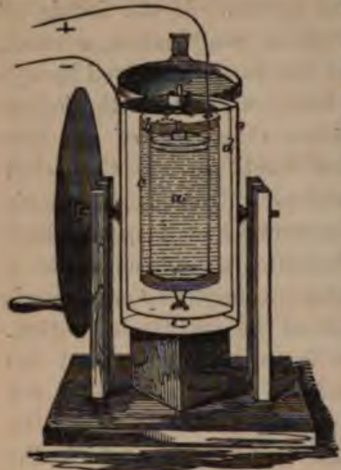
Scarcely any molecular change can take place without either evolution or absorption of heat. When a gas or a vapour becomes liquefied or solidified, the change of state is always attended by the evolution of the heat which it previously contained in a latent state (164), and the effect is reversed when a solid passes into the liquid or the aeriform condition, heat being then absorbed (162). Now, the instances in which chemical combination takes place, without any alteration in the physical condition of bodies, are rare, and the cases in which the product occupies exactly the same bulk as the bodies from which it was formed, are still more so. When two gaseous elements, like chlorine and hydrogen, unite and form a compound which is not only gaseous, but which occupies the same bulk as the bodies did before their combination, the problem is presented in the simplest form: the heat observed in such a case is due solely to the chemical action; but when the products, though gaseous, occupy a smaller bulk after they have entered into combination,—as when 2 volumes of carbonic oxide unite with 1 volume of oxygen, and form but 2 volumes of carbonic acid,—the heat emitted during the act of combination is due partly to chemical action, and partly also to the condensation which the gases have experienced. When the product assumes the liquid form, as occurs in the formation of water during the combustion of hydrogen in oxygen, the quantity of heat emitted owing to this change in form is still more considerable. When, on the other hand, a solid passes into the aeriform state, as when carbon is converted into carbonic acid, the heat actually observed is less than that which the combination ought really to produce: and the effect is reversed when the solid form is assumed by the product, as when phosphorus becomes oxidized to phosphoric acid; in which case the heat evolved exceeds that really due to the act of combination. But even when no change of state is observed, minor disturbing causes are at work. Supposing it were possible to obtain a direct combination of iodine with a metal, such as iron or zinc; even then, though two solids united to form a third solid, it would not necessarily happen that the whole of the heat emitted was due to the chemical action. If the iodide of zinc, for example, contracted in the act of combination, a small portion of the heat observed would be due to that evolved by the solid in consequence of its change of bulk; whereas, if the iodide occupied a larger space after combination than that of the two elements separately, the heat observed would be less than that resulting from the chemical action: and even if no change of bulk occurred, it might happen that the compound had a specific heat different from that of the original elements, and in such case a slight elevation or depression of temperature might be occasioned, which was not really the chemical result of the act of combination.

From the foregoing statements it is therefore clear that the experimental numbers, however carefully the observations are made, can very rarely yield the actual quantities of heat due to the chemical actions: they are compound results from which the true *calorific equivalents* of the different elements (or heat evolved by the combination of chemical equivalents of the different elements), must be deduced by other means.

(1528) *Early Experiments.*—The importance of determining accurately the amount of heat arising from chemical action, was first distinctly announced by Lavoisier, who instituted a series of experiments with the view of finding the quantity of heat evolved during the combustion of various substances: his method consisted in ascertaining the quantity of ice which was melted, when given weights of these bodies were burned in his calorimeter. The first experiments with any claim to accuracy, however, are those of Dulong, which have formed the foundation for all subsequent researches upon the subject. Important additional investigations have since been made, particularly by Despretz, and more recently by Andrews, and by Favre and Silbermann.

(1529) *Researches of Andrews.*—The apparatus employed by Andrews in these experiments (*Phil. Mag.*, May, 1848), was of a simple kind. When the substances to be combined were in the gaseous state, and the products of combustion were also gaseous, the two gases were mixed in the proper proportions, as in the performance of a eudiometric experiment, and introduced into a vessel of thin sheet copper (*a*, Fig. 366), of a capacity of about 24 cubic inches. It was closed by a screw, the head of which was perforated to admit a cork, through which a silver wire, *b*, passed; this wire was connected by a thin platinum wire within the vessel to a second silver wire soldered to the screw itself. The platinum wire could be ignited by connecting it for an instant with a small voltaic battery, and thus the gaseous mixture could be detonated at the pleasure of the operator. The copper vessel containing the mixed gases was then introduced into a larger vessel, *c*, which was filled up with water; the vessel, *c*, was suspended in a cylinder, *d*, provided with a moveable cover, and the whole was enclosed in an outer cylindrical vessel, *e*, arranged so as to admit of its being made to rotate upon its shorter axis.

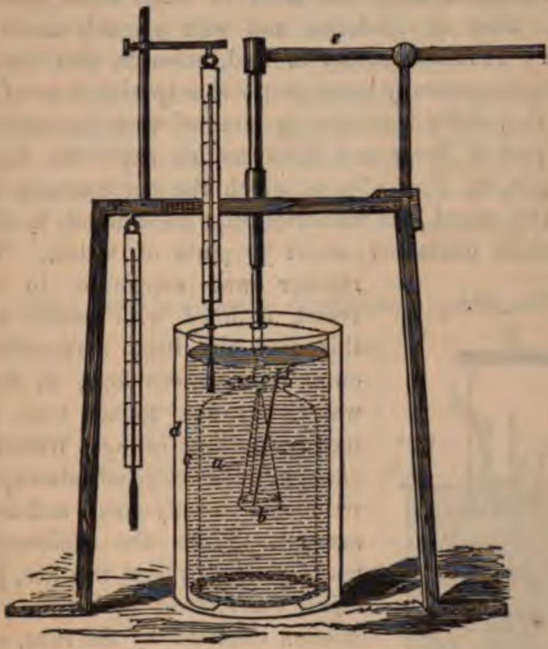
Fig. 366.



The apparatus having been mounted, was caused to rotate, in order to bring every part to a uniform temperature; after which the exact amount of this initial temperature was read off by a very sensitive thermometer, capable of indicating differences of temperature of $\frac{1}{500}$th of a degree Centigrade. The thermometer was then withdrawn, and the gases exploded by igniting the fine platinum wire; the outer vessel of water was closed by a cork, and the apparatus was caused to rotate for thirty-five seconds, in order to establish an equilibrium of temperature in all its parts. The thermometer was again introduced, and the rise of temperature was ascertained. After this observation the apparatus was again made to rotate for thirty-five seconds, and the loss of heat thus occasioned was ascertained. This third rotation was necessary in order to determine the cooling effect of the atmosphere upon the apparatus, during the time that the experiment lasted: in these cases it seldom amounted to more than $\frac{1}{400}$th of the total quantity of heat set free.

When solid bodies were burned in oxygen, the form of the apparatus was modified; the combustion was effected in a copper vessel (*a*, Fig. 367), of about 250 cubic inches in capacity, which was filled with oxygen; and a known weight of the combustible was supported in a small platinum dish, *b*; when all was ready, the vessel *a* having been accurately closed, the combustible was ignited by means of a voltaic current sent through a very fine platinum wire in connexion with the insulated wire *f*. Previously to this ignition, the vessel *a* was immersed in a large cylinder, *c*, filled with a known quantity of water, and the whole was surrounded by an outer vessel of tinplate, *d*, to prevent the effects of radiation. The copper vessel could be agitated within the vessel of water by means of the lever, *e*. Particular expedients were required in certain cases to ensure the ignition; thus, in burning zinc filings and other metals in oxygen, a minute portion of phosphorus was employed to kindle the metal; the weight of this piece of phosphorus being known, the heat which it emitted was calculated, and deducted from that observed. In some cases these experiments lasted fifteen or sixteen minutes, so that the correction for the cooling effect of the external air acquired considerable importance.

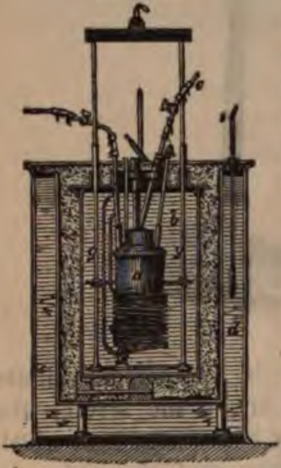
FIG. 367.



When chlorine was used instead of oxygen, it was not necessary to ignite the substance under trial; but in order to prevent the spontaneous ignition of the body, the latter was enclosed in a thin glass bulb, which was broken by agitation of the apparatus at the moment that everything was prepared. The chlorine itself was in most instances contained in a glass vessel, which was filled with the gas by displacement; an excess of the body for combination with the chlorine was always employed, so as to ensure the total absorption of the chlorine. The time allowed for absorption was in each case six minutes and a half.

(1530) *Experiments of Favre and Silbermann.*—A very extensive series of researches upon the development of heat during molecular and chemical changes was undertaken by Favre and Silbermann (*Ann. de Chimie*, III. xxxiv., xxxvi., and xxxvii.). These experiments were conducted in many cases upon a larger scale than those of Andrews, and with a much more elaborate apparatus. It is satisfactory to find, however, that their experimental results generally agree pretty closely with those of Andrews, although they differ from him in some of their deductions. The essential part of Favre and Silbermann's apparatus was a vessel of brass gilt, *a*, Fig. 368, in which the combustions were performed; this vessel was immersed in a calorimeter, *b*, of silvered copper, which contained about $3\frac{1}{4}$ pints of water. The calorimeter was supported in an outer vessel, *c*, lined with swan's down, and this case was itself surrounded by an outer double envelope, *d*, filled with water. It was found that by these means the loss of heat from the influence of the external atmosphere was reduced to a very small and measurable amount. When the combustions were performed in oxygen, this gas, previously dried, was allowed to flow into the combustion chamber by the tube, *e*, and the gases produced, together with the superfluous oxygen, were forced, before their exit from the apparatus, to traverse a spiral tube of thin copper, *f*, so that they might be completely cooled down to the temperature of the water in the calorimeter, *b* : *gg* is an agitator for ensuring uniformity of temperature in the water of the calorimeter.

Fig. 368.



Solid bodies were kindled by the introduction of small pieces of burning charcoal; liquids were burned in small lamps with asbestos wicks, and gases were introduced by a jet previously set on fire. The apparatus in the figure shows the arrangement for burning carbon; the scale of the thermometers employed allowed a variation of $\frac{1}{100}$th of 1° C. to be estimated. In most cases the weight of the substance burned was ascertained by collecting and weighing the products of combustion.

(1531) The following Table is compiled chiefly from the results of Dulong, Andrews, and Favre and Silbermann. It is founded upon the direct results obtained by the rapid combustion, in oxygen, of the various substances enumerated in the first column. The *heat unit* adopted is the one proposed by Dulong, viz., the quantity of heat required to raise one gramme of water 1° C., or rather, from 0° C. to 1° C. The second column indicates the units of heat evolved during the act of combustion; or the weight in grammes of water which would be raised from 0° C. to 1° by the combustion of 1 gramme of each substance. The third column indicates the weight of water heated to the same amount by the combination of 1 gramme of oxygen with each body, and the fourth column (the *calorific equivalent*) is obtained by multiplying the numbers in the third column by 8 (the combining number of oxygen).

Heat developed during Combustion in Oxygen.

Substances burned.	Heat units.		Calorific equivalent.	Compound formed.	Observer.
	Grammes of water raised 1°C., by 1 gramme of each compound	Grammes of water raised 1° C., by combination of 1 gramme of oxygen.	Grammes of water raised 1° C., for 8 grammes (1 eqt.) of oxygen.		
Hydrogen . . .	34462	4307	34462	H_2O_2	Favre & Silbermann.
,, . . .	33808	4226	33808	,,	Andrews.
,, . . .	34743	4343	34743	,,	Dulong.
Carbon	8080	3030	24240	C_2O_4	Favre & Silbermann.
,, ...	7900	2962	23696	,,	Andrews.
,, ...	7912	2967	23736	,,	Despretz.
Sulphur	2220	2220	17760	S_2O_4	Favre & Silbermann.
,, ...	2307	2307	18456	,,	Andrews.
,, ...	2601	2601	20808	,,	Dulong.
Phosphorus . .	5747	4509	36072	PO_5	Andrews.
,, . .	5669			,,	Abria.
Zinc	1301	5285	42282	ZnO	Andrews.
,, ...	1298	5273	42185	,,	Dulong.
Iron	1576	4134	33072	Fe_3O_4	Andrews.
,, ...	1702	4340	34720	,,	Dulong.
Cobalt	1080	3995	31960	?	,,
Nickel	1006	3723	29784	NiO	,,
Tin	1233	4545	36360	SnO_2	,,
,, ...	1144	4230	33519	,,	Andrews.
Antimony . . .	961	5875	47000	SbO_4	Dulong.
Copper	602	2394	19152	CuO	Andrews.
,, . . .	632	2512	20096	,,	Dulong.
Carbonic oxide .	2634	4609	36876	C_2O_4	,,
,, . .	2431	4258	34034	,,	Andrews.
,, . .	2403	4205	33642	,,	Favre & Silbermann
Protoxide of tin .	534	4473	35784	SnO_2	Dulong.
,, .	521	4349	34792	,,	Andrews.

Heat developed during Combustion in Oxygen.

[Continued.]

Substances burned.	Heat units.		Calorific equivalent.		
	Grammes of water raised 1° C., by 1 gramme of each compound	Grammes of water raised 1° C., by combination of 1 gramme of oxygen.	Grammes of water raised 1° C., for 8 grammes (1 eqt.) of oxygen.	Compound formed.	Observer.
Suboxide of copper	256	2288	18304	CuO	Andrews.
"	244	2185	17480	"	Dulong.
Cyanogen . . .	5195	4221	33768		"
Marsh gas . . .	13063	3266	26128		Favre & Silbermann.
" . . .	13185	3296	26368		Dulong.
" . . .	13108	3277	26216		Andrews.
Olefiant gas . .	11942	3483	27864		"
" . .	11858	3458	27664		Favre & Silbermann.
" . .	12030	3514	28112		Dulong.
Alcohol	6909	3311	26488		"
"	6850	3282	26256		Andrews.
"	7183	3442	27536		Favre & Silbermann.
Ether.	9027	3480	27840		" "
Olive oil. . . .	9862				Dulong.
Oil of turpentine .	10852	3294	26352		Favre & Silbermann.
Bisulphide of carbon	3401	2692	21536		" "

The Tables on the following page contain the results of a similar series of experiments, in which chlorine, bromine, and iodine were employed instead of oxygen.

From an inspection of these Tables it may be gathered that the amount of heat disengaged by the following bodies, in their ordinary physical state, during their combination with an equal weight of oxygen, is nearly the same: viz., hydrogen, carbonic oxide, cyanogen, iron, and tin, to which also may be added protoxide of tin, and phosphorus, though the heat disengaged by the body last named is somewhat higher than that furnished by any one of the others. If, however, to these numbers the corrections due to the change in the physical state of the products could be applied, the same coincidence would not be observed; but, although the trustworthy numerical data required for making these corrections do not exist, it is quite obvious that when equivalent quantities of the different elements unite with equal weights of oxygen without undergoing change in their physical state, they emit specific, but different amounts of heat. Sulphur, copper, and protoxide of copper, disengage little more than half the heat of the substances just mentioned, and carbon is intermediate between these two groups. Zinc gives out more heat than either, and potassium more than zinc. . . . .

Quantities of Heat disengaged by the Action of Chlorine.

Elements operated on.	Grammes of water raised 1° C., by combination of 1 gramme of substance.	Grammes of water raised 1° C., by combination of 1 gramme of chlorine.	Grammes of water raised 1° by combination of 1 eqt. (35·5 grammes) of chlorine.	Compound produced.	Observer.
Hydrogen .	24087	678	24087	HCl	Abria.
Hydrogen .	23783	670	23783	"	Favre & Silbermann.
Phosphorus	3422?	607	21548	PCl_5?	Andrews.
Potassium .	2655	2943	104476	KCl	"
Zinc . . .	1529	1427	50658	ZnCl	"
Iron . . .	1745	921	32695	Fe_2Cl_3	"
Tin . . .	1079	897	31722	$SnCl_2$	"
Antimony .	707	860	30401	$SbCl_3$	"
Arsenic . .	994	704	24992	$AsCl_3$	"
Copper . .	961	859	30494	CuCl	"
Mercury .	?	822	29181	?	"

Quantities of Heat disengaged by the Action of Bromine and Iodine.

Elements operated on.	Grammes of water raised 1° C., by combination of 1 gramme of substance.	Grammes of water raised 1° C., by combination of 1 gramme of bromine or iodine.	Grammes of water raised 1° by combination of 1 eqt. of bromine or iodine.	Compound produced.	Observer.
			Bromine.		
Zinc . .	1269	508	40640	ZnBr	Andrews.*
Iron . .	1277	298	23833	Fe_2Br_3	"
			Iodine.		
Zinc . .	819	209	26617	ZnI	"
Iron . .	463	63	8046	Fe_2I_3	"

(1532) *Influence of Dimorphism.*—According to the experiments of Favre and Silbermann, equal weights of the same substance, when in different allotropic conditions, evolve somewhat different amounts of heat during combustion; the modification which is least dense and has the highest specific heat evolving the largest quantity of heat when burned. The following results with carbon, and sulphur, and phosphorus, in different states, may be given in illustration of this point:—

	Units of Heat.	Specific Heat.
Diamond evolves	7770	0·11687
Graphite	7796	0·20187
Wood Charcoal	8080	0·24150

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* *Transactions of the Royal Irish Academy*, vol. xix. 1843.

	Units of Heat.	Specific Heat.
Octohedral Sulphur	2220	0·1776
Prismatic	2264	0·1844
Viscous Sulphur	2258	
Red Phosphorus	5070	0·1700
Vitreous Phosphorus	5953	0·1887

Similar differences were observed when different forms of the same compound body were submitted to experiment. According to these observers, heat was evolved during the conversion of aragonite into calcspar; this is somewhat remarkable, for the density of calcspar is less than that of aragonite, and hence from analogy, an absorption of heat was rather to be looked for in this change.

(1533) *Combustion of Compounds.*— Generally speaking, the heat given out during the combustion of a compound body is less than that emitted by the combustion separately of a quantity of each of its constituents equal in amount to that present in the compound burnt; but this is not uniformly so, as, for instance, in the case of oil of turpentine, and of bisulphide of carbon.

(1534) *Heat evolved in certain Cases during Decomposition.*—In the experiments of Dulong it appeared that when oxide of carbon, or hydrogen, was burned in protoxide of nitrogen, a larger amount of heat was evolved than when the same weights of these gases were burned in oxygen: following up this observation, Favre and Silbermann were led to the remarkable conclusion, that protoxide of nitrogen, in the act of decomposition, evolves a considerable amount of heat; and they estimate that not less than 1154 units of heat are evolved in the separation into its elements of a quantity of nitrous oxide which contains 1 gramme of oxygen. In the decomposition of peroxide of hydrogen also, heat is evolved instead of being absorbed, and they estimate the heat evolved during the liberation of 1 gramme of oxygen from peroxide of hydrogen at 1363 heat units.

Chemists are also familiar with other cases in which decomposition is attended with disengagement of heat; as when the oxides of chlorine, and the so-called iodide and chloride of nitrogen are decomposed. In these cases evolution of light and heat occurs, although the products of decomposition occupy a larger bulk than the compound which furnishes them. A still more striking evolution of heat attends the explosive decomposition of gun-cotton, although the gases produced occupy many hundred times the volume of the original substance. The latter case is particularly instructive, for it is obvious that the oxygen and carbon, although present in the compound, are each there in a form in which they retain a large share of heat, ready to be evolved when more intimate chemical union occurs; and it is by no means improbable that these apparent anomalies may be due to the apparent decompositions being truly double decompositions, two new bodies being in each case formed. Thus, in the instance of peroxide of hydrogen, the decomposition may be thus represented, $HO,O + HO,O = H_2O_2 + O_2$; where the heat evolved by the union of the two atoms of oxygen may be greater than that absorbed in the decomposition of the peroxide of hydrogen.

(1535) *Combustion of Polymeric and Homologous Compounds.*—Favre and Silbermann have likewise examined the amount of heat developed during the combustion of many hydrocarbons and compound ethers. From these experiments it appears that polymeric bodies do not emit equal amounts of heat during combustion; but that the denser the vapour which they furnish, the smaller is the amount of heat which they evolve in combining with equal weights of oxygen. The following table, which indicates the amount of heat given out by hydrocarbons polymeric with olefiant gas, distinctly shows this:—

		Heat Units.
Olefiant Gas	C_4H_4	11858
Amylene	$C_{10}H_{10}$	11491
Paramylene	$C_{20}H_{20}$	11303
Cetene	$C_{32}H_{32}$	11055
Metamylene	$C_{40}H_{40}$	10928

In homologous compounds, such as the alcohols, and the fatty acids, it was also found that for equal weights of oxygen consumed, the heat of combustion was diminished, the oftener that the group of elements (C_2H_2) entered into the formation of the compound.

Even in metameric bodies, which contain the same number of atoms, and which yield vapours of the same density, the quantity of heat evolved during combustion is not necessarily the same; from which it would appear that differences in the molecular arrangement of the component elements, although the number of the atoms may remain unaltered, may yet produce differences in the amount of heat evolved during oxidation. For example, the following metamerides evolve different quantities of heat:—

		Heat Units.
Propionic acid	$HO,C_6H_5O_3$	4670
Formic ether	C_4H_5O,C_2HO_3	5279
Acetate of methyl	$C_2H_3O,C_4H_3O_3$	5344

(1536) *Indirect Methods of Estimating* Calorific Equivalents.—

The difficulties experienced in effecting the direct combustion of the metals in oxygen, chlorine, iodine, and sulphur, in such a manner as to ensure the perfect conversion of the metal into a given compound, unmixed with any other body of higher or lower degrees of oxidation, &c., are so considerable, that Favre and Silbermann were led to attempt the solution of this problem by indirect means, upon a principle previously suggested and applied by Dr. Woods (*Phil. Mag.*, Oct. 1851). An examination of one of the methods employed in the case of the oxides, will furnish an idea of the general principle upon which they proceeded.

Whenever a metal is acted upon by an acid, or when one metal is employed to precipitate another metal from any of its salts, as when zinc is dissolved in sulphuric acid, or when copper is precipitated by means of zinc from a solution of its sulphate, heat is evolved. The calorific effects thus obtained are, however, complicated results: for several chemical processes concur in each operation, some of these processes being attended with the absorption, others with the evolution of heat. The calorimeter, of course, only measures the difference of these quantities.

Now, if it be assumed that the quantity of heat which is absorbed when a compound is separated into its elements is the same as that evolved in the formation of that compound, it becomes possible to calculate the value of the calorific action of any one particular chemical operation in the entire process, provided that the heat produced or absorbed in the other portions of the process be determined by other experiments. Suppose, for instance, we take the case of the solution of zinc in dilute sulphuric acid—the elevation of temperature observed will be the resultant of the following operations:—

In the first place, heat is evolved by the combination of an equivalent of zinc with one of oxygen. Let this amount of heat $=x$.

Secondly, heat is produced by the solution of the oxide of zinc in sulphuric acid: let this $= a$.

Thirdly, heat is absorbed by the separation of the oxygen and hydrogen during the decomposition of a quantity of water equivalent to that of the zinc dissolved: let this $= b$.

If T be the number of heat units indicated by the rise of temperature observed in the calorimeter, supposing a and b to be known from previous experiments, it is obvious that $x = \mathrm{T} - a + b$.

Experiment shows that T, the heat evolved during the solution of 1 gramme of zinc, is equal to 567·9 heat units. The solution in sulphuric acid of 1 gramme of zinc converted into oxide, gave for a a quantity equal to 335·54: and b, the heat absorbed during the decomposition of a quantity of water equivalent to a gramme of zinc, was found by another experiment to be equal to 1060·39 units, or

$$\frac{34462}{32{\cdot}5} \text{ or } \frac{\text{the calorific equivalent of hydrogen}}{\text{the chemical equivalent of zinc}} = 1060{\cdot}39;$$

consequently, x, the heat attendant on the oxidation of zinc, is thus obtained :—

$$\begin{array}{r} \text{Heat Units.} \\ T = 567{\cdot}90 \\ +b = 1060{\cdot}39 \\ \hline 1628{\cdot}29 \\ -a = 335{\cdot}54 \\ \hline x = 1292{\cdot}75 \\ \hline \end{array}$$

This number agrees very closely with the direct determination by Andrews and by Dulong, both of whom burned the metal in oxygen. The experiments of Andrews would give the number 1301, and those of Dulong 1298. But although the results agree very well in the present instance, the divergences are much greater in the case of iron and of copper.

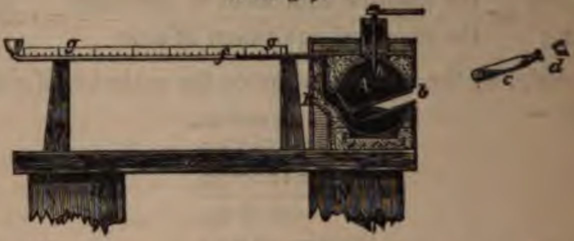
The following are the results deduced by Favre and Silbermann, by operations conducted upon this principle; the quantities of heat evolved being calculated for 1 gramme of each element, when combined with a single equivalent of the bodies with which it is united :—

Elements.	Oxides.	Chlorides.	Bromides.	Iodides.	Sulphides.
Hydrogen . .	34462	23783	9322	—3606	2741
Potassium . .		2587·7	2308	1977·2	1170·8
Sodium . . .		4125·9			
Zinc	1291	1547·5			644·3
Iron	1352·6	1775·5			634·0
Copper . . .	683·9	922·7			285·4
Lead	266·1	430·1	315·4	223·1	91·9
Silver . . .	56·6	322·2	237·2	172·7	51·1

Notwithstanding the confidence with which these numbers are put forward by their authors, it must be admitted that the data necessary for the calculations by which they were obtained are as yet very incomplete. The latent heat of oxygen in the gaseous state is unknown, and other important numbers are wanting: the results given in the foregoing Table cannot, therefore, at present be received without great reserve.

(1537) *Mercurial Calorimeter of Favre and Silbermann.*—Most of these experiments were performed by the aid of a mercurial *calorimeter* (*Ann. de Chimie,* III. xxxvi. 33). This instrument may be regarded as a mercurial thermometer, with a very large bulb capable of receiving within it the substances which were submitted

Fig. 369.



to experiment. It consists of a large glass globe, A, Fig. 369, of the capacity of about 32 fluid ounces, provided with three apertures, one at the top and two at the sides. Into one of the lateral apertures, *b*, is fixed obliquely a tube of thin iron or of platinum, closed at the bottom; and into this tube, which is called the *muffle*, is introduced another tube, *c*, of very thin glass, containing the substances which are to be submitted to experiment: this glass tube is fitted into the metallic tube by means of a cork, *d*; a small quantity of mercury is placed within the muffle, the object of this expedient being to transmit the heat rapidly from the glass tube to the body of the calorimeter. The second lateral aperture, *e*, terminates in a neck which is curved vertically upwards, and into which is cemented the bent extremity of a horizontal capillary tube, *f*, of uniform bore, open at both ends, and 18 or 20 inches in length: by means of this tube the changes in volume of the mercury can be measured upon the scale, *g g*. Through the upper aperture of the globe passes a steel piston, *h*, moved by a screw, by which means the column of mercury in the capillary tube can be reduced at pleasure to the zero of the scale. The globe is itself enclosed in a wooden case, *k*, lined with swan's-down in order to diminish the disturbing effects of external changes of temperature.

The value of the amount of expansion indicated was at once transformed into *units of heat*, by ascertaining the amount of expansion produced by the cooling of a given weight of water from the boiling point, to a measured degree of temperature: by multiplying the weight of water in grammes by the number of degrees Centigrade which it had lost in cooling, the number of *units of heat* was ascertained; since, by our definition, a unit of heat is the quantity of heat required to raise 1 gramme of water 1° C. The number of inches by which the mercurial column had advanced in the capillary tube during the operation was next accurately measured; and by dividing this measured column by the number of heat units, the instrument was graduated so as to enable the observer to record at once the number of units of heat disengaged or absorbed during any chemical change.

This apparatus is good in principle, but it is open to certain objections in the mode of its construction:—the sides of the glass vessel are necessarily thick, to enable it to sustain the large weight of mercury with which it is filled; the glass, therefore, cannot rapidly and certainly adjust itself to the temperature of the hot mercury with which it is in contact. Moreover the tubes are cemented into the three openings with mastic or marine glue. The apparatus, to work well, should have been filled like a barometer or thermometer, since the presence of even a small bubble of air would materially affect the accuracy of the results. It is true that it is stated that the globe was filled with mercury *in vacuo*, but with cemented joints this precaution would soon be rendered useless. It is therefore necessary in estimating the amount of confidence due to the results obtained by its use, to bear in mind these possible sources of inaccuracy. This is the more necessary, since it is principally in the numbers obtained by the use of this apparatus that the results of Favre and Silbermann differ from those of Andrews. At the same time it is to be remarked, that the results published by the French observers appear to be very consistent with each other.

(1538) *On the Heat evolved during Metallic Precipitations.*—On the other hand, it must be stated that the varied and careful experiments of Andrews (*Phil. Trans.* 1848) upon the heat evolved during the precipitation of several metals from their salts by the action of other metals, furnished numerical results differing from those calculated by Favre and Silbermann. In the experiments of Andrews, the corrections required are not in all cases completely under exact experimental control; in the displacement of copper by lead the correction amounts to one-eighth of the whole increment of heat, but in other instances the correction is trifling, not exceeding one-fiftieth of the amount of heat evolved; the numbers obtained are mutually consistent. An additional test of the accuracy of this method is afforded by the data furnished in two different series of experiments upon the amount of heat obtained during the precipitation of copper by zinc—the corresponding numbers in both sets of experiments agreeing very closely with each other. In the first set of experiments metallic copper was precipitated from a strong solution of its sulphate by means of zinc, in a small glass vessel, and the heat estimated by the rise of temperature experienced by the water of a calorimeter in which the glass vessel was contained: in the second series, a dilute solution of sulphate of copper was employed, and the heat was measured by the rise of temperature experienced by the liquid itself. The mean of 4 experiments by the first plan gave 864 as the number of units of heat evolved by the precipitation of each gramme of copper from its sulphate; whilst the mean of 5 experiments upon the latter method was 868.

The following are the numbers given by Andrews, but he has purposely abstained from any attempt to deduce from them the amount of heat developed during the indirect oxidation of the metal which acts as the precipitant:—

Table of Heat evolved during Metallic Precipitations.

Class of Salts used, and Metals employed for precipitating them.	Name of precipitated metal.	Units of heat evolved by precipitated metal.		Name of precipitating metal.	Units of heat for 1 gramme of precipitating metal.
		For 1 gramme.	For 1 equivalent		
Salts of Copper by Zinc .	Copper	866	27452	Zinc	847
Salts of Copper by Iron .	Copper	592	18736	Iron	677
Salts of Copper by Lead .	Copper	268	8488	Lead	82
Salts of Silver by Zinc .	Silver	426	45976	Zinc	1420
Salts of Silver by Copper	Silver	161	17408	Copper	549
Salts of Lead by Zinc . .	Lead	182	18856	Zinc	585
Salts of Mercury by Zinc	Mercury	333	33328	Zinc	1034
Salts of Platinum by Zinc	Platinum	899	88680	Zinc	2750

In these experiments a known weight of finely divided zinc, iron, lead, or copper, as the case might require, was mixed with a solution of the salt to be decomposed; taking care that the metal employed was always more than sufficient completely to decompose the salt in solution: the rise of temperature which occurred was noted with the usual precautions.

Andrews states, as the result of a large number of experiments, that the quantity of heat developed during the mutual action of the same pair of metals is the same, when an equivalent of one metal, A, displaces another metal, B, from any of its salts, whatever may be the acid of the salt employed, provided that B is in the same state of oxidation in each of the compounds submitted to experiment. But if a different metal be employed to effect the precipitation, the amount of heat evolved is different. Thus, whether chloride, or sulphate, or acetate, or formiate of copper be precipitated by zinc, the quantity of heat developed in each case for every equivalent of copper is sensibly the same, viz., 27452. But if iron be substituted for zinc in the precipitation of the copper, the amount of heat is different, viz., 18736; though iron evolves the same amount of heat, whether the sulphate or the chloride of copper be employed. The principle, that the quantity of heat developed during the mutual action of the same pair of metals is always the same whatever be the nature of the acid contained in the salts employed, has since been assumed by Favre and Silbermann in their calculations. If the metals be arranged in a list, beginning with those which emit the largest amount of heat when used as precipitants, the order in which they will stand is the following—zinc, iron, lead, copper, mercury, silver, and platinum. Now, it will be remarked that this is exactly in the electro-chemical order, zinc being the most electro-positive, and platinum the most electro-negative. Another interesting point of connexion between the thermal and the electrical phenomena exhibited by the metals, is to be observed in the fact that the nature of the acid contained in the salt which is undergoing decomposition, does not influence either its thermal equivalent, or the electro-motive force (228), which it exerts when employed in the production of voltaic action.

The following remarkable conclusion was deduced by Andrews from these experiments:—If three metals, A, B, and C, be so related that A is capable of displacing B and C from their combinations, and B be also capable of displacing C, the heat developed by the substitution of A for C will be exactly equal to that developed in the substitution of A for B, together with that developed in the substitution of B for C:—

Heat Units.
Thus, 1 equivalent of lead displaced by zinc = 18856
1 equivalent of copper by lead . . = 8488

1 equivalent of copper by zinc . . = 27344

The experimental number for copper by zinc being 27452

An analogous phenomenon is observed in the electrical relations of the metals (228): when three metals such as platinum, zinc, and potassium are arranged two and two in their electrical order, the electro-motive force generated between the two extremes, platinum and potassium, is equal to the sum of the electro-motive forces of the pairs platinum and zinc, and zinc and potassium.

(1539) *Calorific Equivalents of the Elements.*—The results obtained by the direct action of oxygen, chlorine, iodine, and bromine upon various elementary bodies, are summed up in the following Table, in which the numbers given indicate the quantity of heat evolved by the union of equivalent quantities of oxygen, chlorine, iodine, and bromine, with each element, taking as the standard of comparison, the number of grammes of water at 0° C., which would be raised to 1° C., by the combustion of 1 gramme of hydrogen in oxygen. The quantities of heat thus given out are termed by Favre and Silbermann, the *calorific equivalents* of the different elements.

The numbers to which an A is prefixed are those of Andrews; F. S. indicate those of Favre and Silbermann: when an asterisk is prefixed to any number, the result has been calculated by indirect methods, upon the principle already explained (p. 906):—

Calorific Equivalents of various Elements.

Elements.	Observers.	Oxygen.	Chlorine.	Bromine.	Iodine.	Sulphur.
Hydrogen . .	F.S.	34462	23783	*9322	*—3606	*2741
Carbon . . .	"	24240				
Sulphur . .	"	17760				
Phosphorus .	A.	36072				
Potassium . .	A.		104476			
Ditto . . .	F.S.		*100960	*90188	*77268	*45638
Sodium . .	"		94847			
Zinc . . .	A.	42282	50658	40640	26617	
Ditto . . .	F.S.	*42451	*50296			*20940
Iron	A.	33072	32695	23833	8046	
Ditto . . .	F.S.	*37828	*49651			*17753
Tin	A.	33519	31722			
Arsenic . .			24992			
Antimony . .	Dulong.	47000	A. 30401			
Copper . . .	"	19152	30404			
Ditto . . .	F.S.	*21885	*29524			*9133
Lead . . .	"	*27675	*44730	*32802	*23208	*9556
Silver . . .	"	*6113	*34800	*25618	*18651	*5524

Heat Units evolved by the Combination of 1 Equivalent

	ANDREWS.									FAVRE
Acids.	Potash.	Soda.	Baryta.	Ammonia.	Magnesia.	Lime.	Zinc.	Lead.	Silver.	Potash.
Sulphuric .	15900	16200	...	13900	18500	...	11800	...	...	16083
Sulphurous .	15900	...	...	...	...	...	...	...	...	—
Nitric . .	14600	14000	14700	12200	17700	15700	10300	8900	6900	15510
Phosphoric .	14200	14000	...	...	...	15500	...	...	...	17766
Arsenic . .	14100	13900	...	12200	...	...	...	...	...	...
Hydrochloric	14300	14700	14700	12200	17700	...	10600	...	...	15646
Hydrobromic	...	...	...	...	...	...	...	...	...	15510
Hydriodic .	14200	14100	14700	11900	...	...	9800	...	...	15698
Chromic . .	14000	...	...	...	...	...	...	...	...	...
Oxalic . .	14400	14600	...	12400	...	...	...	...	...	14156
Acetic . .	13800	13800	13700	11900	...	15300	...	8100	...	13975
Formic . .	13900	...	...	...	...	...	...	...	...	...
Tartaric . .	13200	12900	...	11200	...	...	...	...	...	13475
Citric . .	13200	12900	...	11000	...	...	...	...	...	13658
Succinic . .	13400	12900	...	11200	...	...	...	...	...	...

From an examination of the foregoing Table of calorific equiva- nts, it will be obvious that the temperature evolved in the act of com- ination rises highest in those cases in which the chemical affinity etween the two elements is the strongest, and where the compound ossesses the greatest stability. No definite quantitative expression f the law which regulates the evolution of heat during combination, an, however, be deduced from these numbers, owing to the variety f disturbing causes (1478) when bodies are compared in the solid state.

(1540) *On the Heat developed during the Combination of Acids ith Bases.*—A careful and extensive series of experiments upon he heat developed during the saturation of dilute solutions of ifferent acids, by each of the more important bases with which hey form soluble compounds, was published by Andrews in 1841. *Trans. Roy. Irish Acad.*, vol. xix. Part II.) In these experiments, slight excess of acid was purposely employed; the bases, where t was possible, being in a state of solution. When the bases re in the insoluble form, the heat observed is of course lower than hat due to the chemical action; a portion being absorbed in the passage of the base from the solid to the liquid condition; but although the quantity of heat so absorbed is unknown, this amount is constant for the same base, and therefore the observed results obtained for the combination of equal weights of this base with different acids are mutually comparable. A *résumé* of this subject is given by the same author in a "Report on the Heat of Combination," published in the *Report of the British Association* for 1849, p. 69. From these experiments it appears :—

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dermentioned Bases with 1 Equivalent of certain Acids.

AND SILBERMANN.											
Ammonia.	Magnesia.	Lime.	Zinc.	Manganese.	Nickel.	Cobalt.	Iron protox.	Cadmium.	Copper.	Lead.	Silver.
14690	14440	...	10455	12075	11932	11780	10872	10240	7720	...	...
...	...	...	...	...	...	...	...	...	...	...	...
13676	12840	16943	8323	10850	10450	9956	9648	8116	6400	9240	6206
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
13536	13220	...	8307	11235	10412	10374	9828	8109	6416	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
12649	12270	...	7720	9982	9245	9272	8590	7546	5264	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...

1. "That an equivalent of the same base, combined with different acids, produces *nearly* the same quantity of heat.

2. "An equivalent of the same acid, combined with different bases, produces different amounts of heat.

3. "When a neutral salt is converted into an acid salt by combining with one or more equivalents of an acid, no disengagement of heat occurs.

4. "When a double salt is formed by the union of two neutral salts, no disengagement of heat occurs.

5. "When a neutral salt is converted into a basic salt, the combination is accompanied by the disengagement of heat.

6. "When one and the same base displaces another from any of its neutral combinations, the heat evolved or absorbed is always [nearly] the same, whatever the acid element may be."*

The results of Favre and Silbermann lead substantially to similar conclusions, though the absolute quantities of heat which they obtained, in many cases differ considerably from those published by Andrews. The Table which is given on the preceding page indicates the amount of heat obtained by both observers by combining 1 equivalent of each of the different bases, with each acid, the acid being always very slightly in excess.

In the present stage of our knowledge upon this subject, it appears safest to state, that the quantity of heat emitted during the act of combination of equivalent quantities of different acids with a given base, although nearly the same, is not rigidly so. They might probably be arranged in *isothermic* groups, as follows, —those which stand first evolving most heat:—

	With 1 Eqt. of Potash.
1. Sulphuric and sulphurous acids . . .	15900
2. Oxalic, nitric, phosphoric, arsenic, hydrochloric, hydriodic	14600—14200
3. Chromic, formic, acetic	14000—13800
4. Tartaric, citric, succinic.	13200

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* The author cannot here omit acknowledging the kindness of his friend Dr. Andrews, who has furnished him with a Table of his experimental results, reduced from the paper in the *Transactions of the Royal Irish Academy* to the hydrogen unit, corrected for the specific heat of the solutions employed; this correction is very trifling in amount, but it was omitted, as stated, in the original paper. Dr. Andrews has also communicated to the author the result of an unpublished series of experiments upon this subject, which were undertaken with a view of throwing light upon the difference between the conclusions arrived at by the French chemists, and those formerly published by the Professor of Belfast. The general result of these new experiments, which were performed with thermometers of greater delicacy than on the former occasion, and with additional precautions to avoid error, confirms the conclusions previously arrived at by Dr. Andrews.

The bases also differ in the amounts of heat which they emit in combining with the same acid, but as only a very few of the bases are soluble in water, their thermic powers cannot be compared in so simple a manner as those of the acids. Potash, soda, and baryta seem to be nearly isothermic, whilst ammonia is decidedly inferior to these bases. Lime, magnesia, and the other insoluble oxides cannot be satisfactorily compared with each other, until the amount of heat which is absorbed during their passage into the liquid form is known.

(1541) *Quantitative Estimate of Heat absorbed during Solution.*—During the solution of saline bodies in water, heat is generally absorbed; but in a few cases where anhydrous salts are dissolved, an evolution of heat occurs, owing to the formation of a solid hydrate. The following are experimental data furnished by Favre and Silbermann upon this point:—

Heat Absorbed or Evolved during the Solution of Salts.

Name of Salt.	Equivalents.	Heat units absorbed by 1 gramme.	Heat absorbed by 1 Eqt. in grammes.
Sulphate of potash	87×2	35·3	6142
„ soda	71×2	49·1	6972
„ ammonia	66×2	11·1	1465
„ zinc	80·5×2	14·8	2383
„ protoxide of iron . . .	76×2	12·1	1839
„ potash-alum	258·5	23·1	5991
„ ammonia-alum	237·5	19·0	4512
Bisulphate of potash	136	25·6	3481
Chloride of potassium	74·5	51·9	3866
„ sodium	58·5	8·9	520
„ ammonium	53·5	65·1	3483
„ calcium	55·5	15·5	860
„ strontium	79·2	24·9	1972
„ barium	104·0	16·9	1757
Bromide of potassium	119	37·8	4498
Iodide of potassium	166	29·2	4847
Nitrate of potash	101	70·5	7121
„ soda	85	45 5	3867
„ ammonia	80	65·9	5272
„ lime	82	27 1	2222
„ strontia	105·7	41 2	4355
„ lead	165·6	14·9	2467
„ silver	170	31·1	5287

(1542) *Evolution of Heat by the Condensation of Gases.*—During the solution of gaseous acids and bases in water, a considerable evolution of heat takes place, which has been estimated by Favre and Silbermann in the following instances:—

Name of Gas.	Formulæ	Equivalents.	Heat units from 1 gramme.	Heat units from 1 Eqt. in grammes.
Sulphurous acid	SO_2	32	120·4	7705
Hydrochloric acid.	HCl	36·5	449·6	16410
Hydrobromic acid	HBr	81	235·6	19083
Hydriodic acid	HI	128	147·7	18906
Ammonia.	H_3N	17	514·3	8738

APPENDIX.

c Gravities corresponding to Degrees of Baumé's Hydrometer for Liquids heavier than Water.

Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
1·000	20	1·152	40	1·357	60	1·652
1·007	21	1·160	41	1·369	61	1·670
1·013	22	1·169	42	1·382	62	1·689
1·020	23	1·178	43	1·395	63	1·708
1·027	24	1·188	44	1·407	64	1·727
1·034	25	1·197	45	1·420	65	1·747
1·041	26	1·206	46	1·434	66	1·767
1·048	27	1·216	47	1·448	67	1·788
1·056	28	1·225	48	1·462	68	1·809
1·063	29	1·235	49	1·476	69	1·831
1·070	30	1·245	50	1·490	70	1·854
1·078	31	1·256	51	1·495	71	1·877
1·085	32	1·267	52	1·520	72	1·900
1·094	33	1·277	53	1·535	73	1·924
1·101	34	1·288	54	1·551	74	1·949
1·109	35	1·299	55	1·567	75	1·974
1·118	36	1·310	56	1·583	76	2·000
1·126	37	1·321	57	1·600		
1·134	38	1·333	58	1·617		
1·143	39	1·345	59	1·634		

ific Gravities on Baumé's Scale for Liquids lighter than Water.

Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
1·000	23	0·918	36	0·849	49	0·789
0·993	24	0·913	37	0·844	50	0·785
0·986	25	0·907	38	0·839	51	0·781
0·980	26	0·901	39	0·834	52	0·777
0·973	27	0·896	40	0·830	53	0·773
0·967	28	0·890	41	0·825	54	0·768
0·960	29	0·885	42	0·820	55	0·764
0·954	30	0·880	43	0·816	56	0·760
0·948	31	0·874	44	0·811	57	0·757
0·942	32	0·869	45	0·807	58	0·753
0·936	33	0·864	46	0·802	59	0·749
0·930	34	0·859	47	0·798	60	0·745
0·924	35	0·854	48	0·794		

The degrees of Twaddell's hydrometer are readily converted into their corresponding specific gravities by multiplying them by 5, and adding 1000. The following is a short Table of

Degrees on Twaddell's Hydrometer, and the corresponding Specific Gravities.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
1	1·005	8	1·040	15	1·075	22	1·110
2	1·010	9	1·045	16	1·080	23	1·115
3	1·015	10	1·050	17	1·085	24	1·120
4	1·020	11	1·055	18	1·090	25	1·125
5	1·025	12	1·060	19	1·095	26	1·130
6	1·030	13	1·065	20	1·100	27	1·135
7	1·035	14	1·070	21	1·105	28	1·140

English Weights and Measures.—Avoirdupois.

	Grains.	Drachms.	Ounces.	lb.	Qrs.	Cwt.	Tons.
Grain . .	1						
Drachm .	27·34	1					
Ounce .	437·5	16	1				
Pound .	7000	256	16	1			
Quarter .	196000	7168	448	28	1		
Cwt. . .	784000	28672	1792	112	4	1	
Ton . .	15680000	573440	35840	2240	80	20	1

Troy Weight.

	Grains.	Dwts.	Ounces.	lb.
Grain	1			
Pennyweight . .	24	1		
Ounce	480	20	1	
Pound	5760	240	12	1

1 cubic inch of distilled water in air at 62° F. = 252·456 grains.
1 cubic inch of distilled water *in vacuo* at 62° F. = 252·722 grains.

		Cubic Inches.
1 Gallon	=	277·276
1 Pint	=	34·659
1 Fluid ounce	=	1·7329
1 Litre	=	61·024
1 Cubic centimetre	=	0·061024

1 Cubic inch = 16·387 cubic centimetres.

1·00000 parts of gas at 32° F., 29·922 Bar. (also at 32°), become at 60° F., Bar. 30 inches (also at 60°) = 1·05720 parts.

Comparison of French and English Weights.

	Grains.		Grains.
1 Gramme* =	15·432348	6 Grammes =	92·594088
2 " =	30·864696	7 " =	108·026436
3 " =	46·297044	8 " =	123·458784
4 " =	61·729392	9 " =	138·891132
5 " =	77·161740	10 " =	154·323480

The weight of a gramme is that of a cubic centimetre of distilled water at 39°·2 F.

		Grains.		Oz. Av.		lb. Av.
1 Milligramme	=	0·01543				
1 Centigramme	=	0·15432				
1 Decigramme	=	1·5432				
1 Gramme	=	15·432				
1 Kilogramme	=	15432·348	=	35·2739	=	2·2046

Comparison of French and English Measures of Length.

		English Inches.		Feet.		Yards.
1 Millimetre	=	0·03937079				
1 Centimetre	=	0·3937079				
1 Decimetre	=	3·937079				
1 Metre†	=	39·37079	=	3·280899	=	1·093633
1 Kilometre	=	39370·79	=	3280·899	=	1093·633

The length of the platinum metre is estimated at the temperature of 32° F., the English standard yard at 62° F.

1 English inch is equal to 25·4 millimetres.

		Fluid ounces.		Pints.
1 Litre	=	35·2754	=	1·76377

The capacity of a litre is that of a cube, each side of which is a decimetre.

To Reduce Grammes to Grains.

Log. Grammes + 1·188432 = log. Grains.

To Reduce Cubic Centimetres to Cubic Inches.

Log. cubic centimetres + (−2·7855007) = log. Cubic inches.

To Reduce Millimetres to Inches.

Log. millimetres + (−2·5951663) = log. inches.

To Convert Grains into Grammes.

Log. grains + (−2·8115680) = log. grammes.

To Convert Cubic Inches into Cubic Centimetres.

Log. cubic inches + 1·2144993 = log. cubic centimetres.

To Convert Inches into Millimetres.

Log. inches + 1·4048337 = log. millimetres.

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* This determination of the gramme was made from the kilogramme des Archives by Professor W. H. Miller, in fixing the national standards (*Phil. Trans.* 1856, p. 893).

† The metre is a ten-millionth part of a quadrant of a meridian circle of the earth.

Values of Millimetres in English Inches.

Millimetres.	English inches.	Millimetres.	English inches.	Millimetres.	English inches.
1	0·03937079	45	1·7716	125	4·941
2	0·07874158	50	1·968	130	5·118
3	0·11811237	55	2·165	135	5·315
4	0·15748316	60	2·362	140	5·512
5	0·19685395	65	2·559	145	5·708
6	0·23622474	70	2·756	150	5·906
7	0·27559553	75	2·953	155	6·103
8	0·31496632	80	3·149	160	6·299
9	0·35433711	85	3·346	165	6·496
10	0·39370790	90	3·543	170	6·693
15	0·5905	95	3·740	175	6·890
20	0·7874	100	3·937	180	7·087
25	0·9842	105	4·134	185	7·284
30	1·1811	110	4·331	190	7·480
35	1·3779	115	4·528	195	7·677
40	1·5748	120	4·744	200	7·874

Table of the corresponding Heights of the Barometer in Millimetres and English Inches.

Millimetres.		English inches.	Millimetres.		English inches.	Millimetres.		English inches.
720	=	28·347	739	=	29·095	758	=	29·843
721	=	28·386	740	=	29·134	759	=	29·882
722	=	28·425	741	=	29·174	760	=	29·922
723	=	28·465	742	=	29·213	761	=	29·961
724	=	28·504	743	=	29·252	762	=	30·000
725	=	28·543	744	=	29·292	763	=	30·039
726	=	28·583	745	=	29·331	764	=	30·079
727	=	28·622	746	=	29·370	765	=	30·118
728	=	28·662	747	=	29·410	766	=	30·158
729	=	28·701	748	=	29·449	767	=	30·197
730	=	28·740	749	=	29·488	768	=	30·236
731	=	28·780	750	=	29·528	769	=	30·276
732	=	28·819	751	=	29·567	770	=	30·315
733	=	28·858	752	=	29·606	771	=	30·355
734	=	28·898	753	=	29·645	772	=	30·394
735	=	28·937	754	=	29·685	773	=	30·433
736	=	28·976	755	=	29·724	774	=	30·473
737	=	29·016	756	=	29·764	775	=	30·512
738	=	29·055	757	=	29·803			

able for the Conversion of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
−100	−148·0	−49	−56·2	2	35·6	53	127·4
−99	−146·2	−48	−54·4	3	37·4	54	129·2
−98	−144·4	−47	−52·6	4	39·2	55	131·0
−97	−142·6	−46	−50·8	5	41·0	56	132·8
−96	−140·8	−45	−49·0	6	42·8	57	134·6
−95	−139·0	−44	−47·2	7	44·6	58	136·4
−94	−137·2	−43	−45·4	8	46·4	59	138·2
−93	−135·4	−42	−43·6	9	48·2	60	140·0
−92	−133·6	−41	−41·8	10	50·0	61	141·8
−91	−131·8	−40	−40·0	11	51·8	62	143·6
−90	−130·0	−39	−38·2	12	53·6	63	145·4
−89	−128·2	−38	−36·4	13	55·4	64	147·2
−88	−126·4	−37	−34·6	14	57·2	65	149·0
−87	−124·6	−36	−32·8	15	59·0	66	150·8
−86	−122·8	−35	−31·0	16	60·8	67	152·6
−85	−121·0	−34	−29·2	17	62·6	68	154·4
−84	−119·2	−33	−27·4	18	64·4	69	156·2
−83	−117·4	−32	−25·6	19	66·2	70	158·0
−82	−115·6	−31	−23·8	20	68·0	71	159·8
−81	−113·8	−30	−22·0	21	69·8	72	161·6
−80	−112·0	−29	−20·2	22	71·6	73	163·4
−79	−110·2	−28	−18·4	23	73·4	74	165·2
−78	−108·4	−27	−16·6	24	75·2	75	167·0
−77	−106·6	−26	−14·8	25	77·0	76	168·8
−76	−104·8	−25	−13·0	26	78·8	77	170·6
−75	−103·0	−24	−11·2	27	80·6	78	172·4
−74	−101·2	−23	−9·4	28	82·4	79	174·2
−73	−99·4	−22	−7·6	29	84·2	80	176·0
−72	−97·6	−21	−5·8	30	86·0	81	177·8
−71	−95·8	−20	−4·0	31	87·8	82	179·6
−70	−94·0	−19	−2·2	32	89·6	83	181·4
−69	−92·2	−18	−0·4	33	91·4	84	183·2
−68	−90·4	−17	+1·4	34	93·2	85	185·0
−67	−88·6	−16	3·2	35	95·0	86	186·8
−66	−86·8	−15	5·0	36	96·8	87	188·6
−65	−85·0	−14	6·8	37	98·6	88	190·4
−64	−83·2	−13	8·6	38	100·4	89	192·2
−63	−81·4	−12	10·4	39	102·2	90	194·0
−62	−79·6	−11	12·2	40	104·0	91	195·8
−61	−77·8	−10	14·0	41	105·8	92	197·6
−60	−76·0	−9	15·8	42	107·6	93	199·4
−59	−74·2	−8	17·6	43	109·4	94	201·2
−58	−72·4	−7	19·4	44	111·2	95	203·0
−57	−70·6	−6	21·2	45	113·0	96	204·8
−56	−68·8	−5	23·0	46	114·8	97	206·6
−55	−67·0	−4	24·8	47	116·6	98	208·4
−54	−65·2	−3	26·6	48	118·4	99	210·2
−53	−63·4	−2	28·4	49	120·2	100	212·0
−52	−61·6	−1	30·2	50	122·0	101	213·8
−51	−59·8	0	32·0	51	123·8	102	215·6
−50	−58·0	+1	33·8	52	125·6	103	217·4

Conversion of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

[*Continued.*]

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
104	219·2	155	311·0	206	402·8	257	494·6
105	221·0	156	312·8	207	404·6	258	496·4
106	222·8	157	314·6	208	406·4	259	498·2
107	224·6	158	316·4	209	408·2	260	500·0
108	226·4	159	318·2	210	410·0	261	501·8
109	228·2	160	320·0	211	411·8	262	503·6
110	230·0	161	321·8	212	413·6	263	505·4
111	231·8	162	323·6	213	415·4	264	507·2
112	233·6	163	325·4	214	417·2	265	509·0
113	235·4	164	327·2	215	419·0	266	510·8
114	237·2	165	329·0	216	420·8	267	512·6
115	239·0	166	330·8	217	422·6	268	514·4
116	240·8	167	332·6	218	424·4	269	516·2
117	242·6	168	334·4	219	426·2	270	518·0
118	244·4	169	336·2	220	428·0	271	519·8
119	246·2	170	338·0	221	429·8	272	521·6
120	248·0	171	339·8	222	431·6	273	523·4
121	249·8	172	341·6	223	433·4	274	525·2
122	251·6	173	343·4	224	435·2	275	527·0
123	253·4	174	345·2	225	437·0	276	528·8
124	255·2	175	347·0	226	438·8	277	530·6
125	257·0	176	348·8	227	440·6	278	532·4
126	258·8	177	350·6	228	442·4	279	534·2
127	260·6	178	352·4	229	444·2	280	536·0
128	262·4	179	354·2	230	446·0	281	537·8
129	264·2	180	356·0	231	447·8	282	539·6
130	266·0	181	357·8	232	449·6	283	541·4
131	267·8	182	359·6	233	451·4	284	543·2
132	269·6	183	361·4	234	453·2	285	545·0
133	271·4	184	363·2	235	455·0	286	546·8
134	273·2	185	365·0	236	456·8	287	548·6
135	275·0	186	366·8	237	458·6	288	550·4
136	276·8	187	368·6	238	460·4	289	552·2
137	278·6	188	370·4	239	462·2	290	554·0
138	280·4	189	372·2	240	464·0	291	555·8
139	282·2	190	374·0	241	465·8	292	557·6
140	284·0	191	375·8	242	467·6	293	559·4
141	285·8	192	377·6	243	469·4	294	561·2
142	287·6	193	379·4	244	471·2	295	563·0
143	289·4	194	381·2	245	473·0	296	564·8
144	291·2	195	383·0	246	474·8	297	566·6
145	293·0	196	384·8	247	476·6	298	568·4
146	294·8	197	386·6	248	478·4	299	570·2
147	296·6	198	388·4	249	480·2	300	572·0
148	298·4	199	390·2	250	482·0	301	573·8
149	300·2	200	392·0	251	483·8	302	575·6
150	302·0	201	393·8	252	485·6	303	577·4
151	303·8	202	395·6	253	487·4	304	579·2
152	305·6	203	397·4	254	489·2	305	581·0
153	307·4	204	399·2	255	491·0	306	582·8
154	309·2	205	401·0	256	492·8	307	584·6

version of Degrees on the Centigrade Thermometer into those of Fahrenheit's Scale.

[Continued.]

° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.	° Cent.	° Fah.
308	586·4	330	626·0	351	663·8	480	896
309	588·2	331	627·8	352	665·6	490	914
310	590·0	332	629·6	353	667·4	500	932
311	591·8	333	631·4	354	66 92	600	1112
312	593·6	334	633·2	355	67 10	700	1292
313	595·4	335	635·0	356	672·8	800	1472
314	597·2	336	636·8	357	674·6	900	1652
315	599·0	337	638·6	358	676·4	1000	1832
316	600·8	338	640·4	359	678·2	1100	2012
317	602·6	339	642·2	360	680·0	1200	2192
318	604·4	340	644·0	370	698	1300	2372
319	606·2	341	645·8	380	716	1400	2552
320	608·0	342	647·6	390	734	1500	2732
321	609·8	343	649·4	400	752	1600	2912
322	611·6	344	651·2	410	770	1700	3092
323	613·4	345	653·0	420	788	1800	3272
324	615·2	346	654·8	430	806	1900	3452
325	617·0	347	656·6	440	824	2000	3632
326	618·8	348	658·4	450	842	2100	3812
327	620·6	349	660·2	460	860	2200	3922
328	622·4	350	662·0	470	878	2300	4172
329	624·2						

Quantities of Absolute Alcohol by Weight, in Mixtures of Alcohol and Water of the following Specific Gravities (*Drinkwater*) :—

Specific Gravity at 60° F.	Alcohol by weight in 100 parts.	Specific Gravity at 60° F.	Alcohol by weight in 100 parts.	Specific Gravity at 60° F.	Alcohol by weight in 100 parts.	Specific Gravity at 60° F.	Alcohol by weight in 100 parts.	Specific Gravity at 60° F.	Alcohol by weight in 100 parts.
1·0000	0·00	0·9967	1·78	·9934	3·67	·9901	5·70	·9869	7·85
·9999	0·05	·9966	1·83	·9933	3·73	·9900	5·77	·9868	7·92
·9998	0·11	·9965	1·89	·9932	3·78	·9899	5·83	·9867	7·99
·9997	0·16	·9964	1·94	·9931	3·84	·9898	5·89	·9866	8·06
·9996	0·21	·9963	1·99	·9930	3·90	·9897	5·96	·9865	8·13
·9995	0·26	·9962	2·05	·9929	3·96	·9896	6·02	·9864	8·20
·9994	0·32	·9961	2·11	·9928	4·02	·9895	6·09	·9863	8·27
·9993	0·37	·9960	2·17	·9927	4·08	·9894	6·15	·9862	8·34
·9992	0·42	·9959	2·22	·9926	4·14	·9893	6·22	·9861	8·41
·9991	0·47	·9958	2·28	·9925	4·20	·9892	6·29	·9860	8·48
·9990	0·53	·9957	2·34	·9924	4·27	·9891	6·35	·9859	8·55
·9989	0·58	·9956	2·39	·9923	4·33	·9890	6·42	·9858	8·62
·9988	0·64	·9955	2·45	·9922	4·39	·9889	6·49	·9857	8·70
·9987	0·69	·9954	2·51	·9921	4·45	·9888	6·55	·9856	8·77
·9986	0·74	·9953	2·57	·9920	4·51	·9887	6·62	·9855	8·84
.9985	0·80	·9952	2·62	·9919	4·57	·9886	6·69	·9854	8·91
·9984	0·85	·9951	2·68	·9918	4·64	·9885	6·75	·9853	8·98
·9983	0·91	·9950	2·74	·9917	4·70	·9884	6·82	·9852	9·05
·9982	0·96	·9949	2·79	·9916	4·76	·9883	6·89	·9851	9·12
·9981	1·02	·9948	2·85	·9915	4·82	·9882	6·95	·9850	9·20
·9980	1·07	·9947	2·91	·9914	4·88	·9881	7·02	·9849	9·27
·9979	1·12	·9946	2·97	·9913	4·94	·9880	7·09	·9848	9·34
·9978	1·18	·9945	3·02	·9912	5·01	·9879	7·16	·9847	9·41
·9977	1·23	·9944	3·08	·9911	5·07	·9878	7·23	·9846	9·49
·9976	1·29	·9943	3·14	·9910	5·13	·9877	7·30	·9845	9·56
·9975	1·34	·9942	3·20	·9909	5·20	·9876	7·37	·9844	9·63
·9974	1·40	·9941	3·26	·9908	5·26	·9875	7·43	·9843	9·70
·9973	1·45	·9940	3·32	·9907	5·32	·9874	7·50	·9842	9·78
·9972	1·51	·9939	3·37	·9906	5·39	·9873	7·57	·9841	9·85
·9971	1·56	·9938	3·43	·9905	5·45	·9872	7·64	·9840	9·92
·9970	1·61	·9937	3·49	·9904	5·51	·9871	7·71	.9839	9·99
·9969	1·67	·9936	3·55	·9903	5·58	·9870	7·78	·9838	10·07
·9968	1·73	·9935	3·61	·9902	5·64				

This Table is founded on synthetic experiments, in which eleven different mixtures of alcohol and water were made, containing respectively 0·5, 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 per cent. of alcohol by weight : the alcohol employed had a specific gravity of 0·7938 at 60°.

Proportion of Absolute Alcohol by Weight in 100 *parts of Spirit, of different Specific Gravities at* 60° F.

(Fownes. *Phil. Trans.*, 1847.)

Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.
0·5	1·0000	25	·9652	51	·9160	76	·8581
0	·9991	26	·9638	52	·9135	77	·8557
1	·9981	27	·9623	53	·9113	78	·8533
2	·9965	28	·9609	54	·9090	79	·8508
3	·9947	29	·9593	55	·9069	80	·8483
4	·9930	30	·9578	56	·9047	81	·8459
5	·9914	31	·9560	57	·9025	82	·8434
6	·9898	32	·9544	58	·9001	83	·8408
7	·9884	33	·9528	59	·8979	84	·8382
8	·9869	34	·9511	60	·8956	85	·8357
9	·9855	35	·9490	61	·8932	86	·8331
10	·3841	36	·9470	62	·8908	87	·8305
11	·9828	37	·9452	63	·8886	88	·8279
12	·9815	38	·9434	64	·8863	89	·8254
13	·9802	39	·9416	65	·8840	90	·8228
14	·9789	40	·9396	66	·8816	91	·8199
15	·9778	41	·9376	67	·8793	92	·8172
16	·9766	42	·9356	68	·8769	93	·8145
17	·9753	43	·9335	69	·8745	94	·8118
18	·9741	44	·9314	70	·8721	95	·8089
19	·9728	45	·9292	71	·8696	96	·8061
20	·9716	46	·9270	72	·8672	97	·8031
21	·9704	47	·9249	73	·8649	98	·8001
22	·9691	48	·9228	74	·8625	99	·7969
23	·9678	49	·9206	75	·8603	100	·7938
24	·9665	50	·9184				

In this Table every alternate number is the result of a direct thetical experiment; absolute alcohol and distilled water being ighed out in the proper proportions, and mixed by agitation in ppered bottles; after a lapse of three or four days, each speci- n was brought exactly to 60° F. and the specific gravity termined with great care.

	TYPE, WATER. $n\left.\begin{matrix}H\\H\end{matrix}\right\}O_2$.		TYPE
	OXIDES.	SULPHIDES. (Selenides, tellurides).	CHLORIDES (Bromides,iodides,and
DERIVATIVES from positive radicals.	**Bases,** properly so called. 1. *Primary* or *hydrated bases.* *e.g.* hydrate of potash, $\left.\begin{matrix}K\\H\end{matrix}\right\}O_2$; hydrate of arsenethylium, $\left.\begin{matrix}(C_4H_5)_4As\\H\end{matrix}\right\}O_2$. 2. *Secondary* or *anhydrous bases, e.g.* oxide of potassium, $\left.\begin{matrix}K\\K\end{matrix}\right\}O_2$.	**Sulphides of bases.** 1. *Primary Sulphides,* or *sulphhydrides, e.g.* sulphhydride of potassium, $\left.\begin{matrix}K\\H\end{matrix}\right\}S_2$; sulphhydride of aniline, $\left.\begin{matrix}H_2(C_{12}H_5)N\\H\end{matrix}\right\}S_2$. 2. *Secondary* or *metallic sulphides, e.g.* sulphide of potassium, $\left.\begin{matrix}K\\K\end{matrix}\right\}S_2$	**Chlorides of bas** 1. *Primary* or m *rides,* chloride sium (KCl); by of aniline [H_2(C_{12} . . . .
	Alcohols, or hydrocarburetted bases. 1. *Primary,* or *true alcohols, e.g.* wood spirit, $\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\}O_2$; hydrate of phenyl, $\left.\begin{matrix}C_{12}H_5\\H\end{matrix}\right\}O_2$; glycerin, $\left.\begin{matrix}(C_6H_5)'''\\H_3\end{matrix}\right\}O_6$. 2. *Secondary alcohols or simple ethers, e.g.* ordinary ether, $\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2$.	**Sulphides of alcohols.** 1. *Primary sulphides,* or *mercaptans, e.g.* sulphhydride of ethyl $\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}S_2$. 2. *Secondary sulphides,* or *sulphuretted ethers, e.g.* sulphide of ethyl, $\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}S_2$.	**Chlorides of alc** 1. *Primary chlorid* *chloric ethers, e.* of ethyl (C_4H_5,Cl) . . . .
	Aldehyds. 1. *Primary aldehyds, e.g.* acetic aldehyd, $\left.\begin{matrix}C_4H_3\\H\end{matrix}\right\}O_2$; essence of bitter almonds, $\left.\begin{matrix}C_{14}H_5\\H\end{matrix}\right\}O_2$. 2. *Secondary aldehyds* (examples wanting).	**Sulphides of aldehyds.** 1. *Primary sulphides, e.g.* sulpho-benzol, $\left.\begin{matrix}C_{14}H_5\\H\end{matrix}\right\}S_2$. 2. *Secondary sulphides* (wanting).	**Chlorides of alde** 1. *Primary chlorid* ride of aldehy Dutch liquid) (C . . . .
DERIVATIVES from negative radicals.	**Acids.** 1. *Primary* or *hydrated acids, e.g.* sulphuric, $\left.\begin{matrix}(S_2O_4)''\\H_2\end{matrix}\right\}O_4$, benzoic, $\left.\begin{matrix}C_{14}H_5O_2.\\H\end{matrix}\right\}O_2$, cyanic $\left.\begin{matrix}C_2N\\H\end{matrix}\right\}O_2$, acids. 2. *Secondary* or *anhydrous acids, e.g.* sulphuric, $(S_2O_4)''O_2$, and benzoic, $\left.\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}O_2$; anhydrides.	**Sulphides of acids.** 1. *Primary sulphides, e.g.* hydro-sulphocyanic acid, $\left.\begin{matrix}C_2N\\H\end{matrix}\right\}S_2$. 2. *Secondary sulphides, e.g.* sulphide of benzoyl, $\left.\begin{matrix}C_{14}H_5O_2\\C_{14}H_5O_2\end{matrix}\right\}S_2$.	**Chlorides of acid** 1. *Primary chlorid* *chlorides, e.g.* be chloride, or chlori zoyl ($C_{14}H_5O_2$,Cl); ride of phosphorus free chlorine (Cl,C ride of cyanogen (C . . . .
DERIVATIVES from both positive and negative radicals.	**Oxysalts,** *e.g.* sulphates, $\left.\begin{matrix}(S_2O_4)''\\K_2\end{matrix}\right\}O_4$; nitrates, $\left.\begin{matrix}NO_4\\K\end{matrix}\right\}O_2$; cyanates, $\left.\begin{matrix}Cy\\K\end{matrix}\right\}O_2$. **Compound ethers,** *e.g.* sulphuric ether, $\left.\begin{matrix}(S_2O_4)''\\(C_4H_5)_2\end{matrix}\right\}O_4$; cyanic ether, $\left.\begin{matrix}Cy\\C_4H_5\end{matrix}\right\}O_2$; oxalic ether, $\left.\begin{matrix}(C_4O_4)''\\(C_4H_5)_2\end{matrix}\right\}O_4$; glycerides as tristearin, $\left.\begin{matrix}(C_6H_5)'''\\(C_{36}H_{35}O_2)_3\end{matrix}\right\}O_6$. **Compound aldehyds.**	**Sulpho-salts,** *e.g.* sulphocyanides, $\left.\begin{matrix}Cy\\K\end{matrix}\right\}S_2$; sulphantimoniates, $\left.\begin{matrix}Sb'''\\K\end{matrix}\right\}S_4$. **Compound sulphuretted ethers,** *e.g.* thiacetate of ethyl, $\left.\begin{matrix}C_4H_3O_2\\C_4H_5\end{matrix}\right\}S_2$; sulphocyanide of ethyl, $\left.\begin{matrix}Cy\\C_4H_5\end{matrix}\right\}S_2$. **Compound sulphuretted aldehyds.**	. . . .

IDES.	TYPE, AMMONIA. $\left.\begin{matrix}H\\ nH\\ H\end{matrix}\right\}N.$ NITRIDES. (Phosphides, Arsenides, and Stibides.)	TYPE, HYDROGEN. $\left.\begin{matrix}H\\ {}^{n}H\end{matrix}\right\}$ METALS. (Both simple and compound.)
ases. *etallic cyanides:* potassium (KCy); of potassium,	**Nitrides of bases.** 1. *Primary nitrides: e.g.* amide of potassium, $\left.\begin{matrix}K\\ H\\ H\end{matrix}\right\}N.$	**Metals of bases.** 1. *Primary metals*, or *hydrides of metals: e.g.* hydride of copper, Cu_2H.
. . . . . .	2. *Secondary nitrides:* (unknown as yet.)	2. *Secondary metals*, or *metals properly so called: e.g.* potassium $\left.\begin{matrix}K\\ K\end{matrix}\right\}$; stibiotriethyl, $\left.\begin{matrix}Sb'''\\ (C_4H_5)_3\end{matrix}\right\}$.
. . . . . .	3. *Tertiary nitrides: e.g.* nitride of potassium, $\left.\begin{matrix}K\\ K\\ K\end{matrix}\right\}N.$	
lcohols. *des*, or *hydrocyanic riles: e.g.* acetoni- *r).*	**Nitrides of alcohols,** or bases from alcohols. 1. *Primary nitrides: e.g.* ethylia, $\left.\begin{matrix}C_4H_5\\ H\\ H\end{matrix}\right\}N.$	**Metals of Alcohol.** 1. *Primary metals*, or *hydrides of the alcohols: e.g.* marsh gas, $\left.\begin{matrix}C_2H_3\\ H\end{matrix}\right\}$; benzol $\left.\begin{matrix}C_{12}H_5\\ H\end{matrix}\right\}$.
. . . . . .	2. *Secondary nitrides: e.g.* diethylia, $\left.\begin{matrix}C_4H_5\\ C_4H_5\\ H\end{matrix}\right\}N.$	2. *Secondary metals*, or *alcohol radicles: e.g.* ethyl, $\left.\begin{matrix}C_4H_5\\ C_4H_5\end{matrix}\right\}$ amyl, $\left.\begin{matrix}C_{10}H_{11}\\ C_{10}H_{11}\end{matrix}\right\}$.
. . . . . .	3. *Tertiary nitrides: e.g.* triethylia, $\left.\begin{matrix}C_4H_5\\ C_4H_5\\ C_4H_5\end{matrix}\right\}N.$	
ldehyds. *ides:* (not known	**Nitrides of aldehyds.** 1. *Primary nitrides.*	**Metals of aldehyds.** 1. *Primary metals*, or *hydrides of aldehyds: e.g.* olefiant gas, $\left.\begin{matrix}C_4H_3\\ H\end{matrix}\right\}$.
. . . . . .	2. *Secondary nitrides.*	2. *Secondary metals:* (not yet obtained).
. . . . . .	3. *Tertiary nitrides.* (All these classes are as yet unknown.)	
cids. *ides: e.g.* cyanide $_{14}H_5O_2$,Cy); free ,Cy).	**Nitrides of acids.** 1. *Primary nitrides: e.g.* benzamide, $\left.\begin{matrix}C_{14}H_5O_2\\ H\\ H\end{matrix}\right\}N$; succinamide, $\left.\begin{matrix}(C_8H_4O_4)''\\ H_2\\ H_2\end{matrix}\right\}N_2.$	**Metals of acids.** 1. *Primary metals*, or *hydro-acids: e.g.* hydride of benzoyl, $\left.\begin{matrix}C_{14}H_5O_2\\ H\end{matrix}\right\}$; hydrochloric acid, $\left.\begin{matrix}Cl\\ H\end{matrix}\right\}$; hydrocyanic acid, $\left.\begin{matrix}Cy\\ H\end{matrix}\right\}$.
. . . . . .	2. *Secondary nitrides: e.g.* succinimide, $\left.\begin{matrix}(C_8H_4O_4)''\\ (C_8H_4O_4)''\\ H_2\end{matrix}\right\}N_2$; hippuric acid, $\left.\begin{matrix}C_4H_3O_4\\ C_{14}H_5O_2\\ H\end{matrix}\right\}N.$	2. *Secondary metals*, or *radicles: e.g.* benzoyl, $\left.\begin{matrix}C_{14}H_5O_2\\ C_{14}H_5O_2\end{matrix}\right\}$; chlorine, $\left.\begin{matrix}Cl\\ Cl\end{matrix}\right\}$; cyanogen, $\left.\begin{matrix}Cy\\ Cy\end{matrix}\right\}$.
. . . . . .	3. *Tertiary nitrides: e.g.* dibenzosalicylamide, $\left.\begin{matrix}C_{14}H_5O_2\\ C_{14}H_5O_2\\ C_{14}H_5O_4\end{matrix}\right\}N$; free nitrogen, N''', N.	
. . . . . .	**Salts of amides:** *e.g.* hydrargobenzamide, $\left.\begin{matrix}C_{14}H_5O_2\\ Hg\\ H\end{matrix}\right\}N.$	In this division many of those already referred to other classes would find their places, such for instance as the cyanides of the alcohols, which contain the electro-negative radicle (cyanogen) of cyanic acid, and the electro-positive radicle of the alcohol.
. . . . . .	**Alkalamides,** or amides derived from alkaloids or organic bases instead of from ammonia: *e.g.* oxanilide, $\left.\begin{matrix}(C_4O_4)''\\ (C_{12}H_5)_2\\ H_2\end{matrix}\right\}N_2$; ethyl-acetamide, $\left.\begin{matrix}C_4H_3O_2\\ C_4H_5\\ H\end{matrix}\right\}N.$	

Table of the Tension of Aqueous Vapour expressed in Inches of Mercury, at 32° F., *for each degree* F. *between* 0° *and* 100.°

Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.	Temp. ° F.	Inches of Mercury.
0	0·0439	26	0·1395	51	0·3742	76	0·8964
1	0·0459	27	0·1457	52	0·3882	77	0·9266
2	0·0481	28	0·1522	53	0·4026	78	0·9577
3	0·0503	29	0·1589	54	0·4175	79	0·9898
4	0·0526	30	0·1660	55	0·4329	80	1·0227
5	0·0551	31	0·1733	56	0·4488	81	1·0566
6	0·0576	32	0·1810	57	0·4653	82	1·0915
7	0·0603	33	0·1883	58	0·4822	83	1·1274
8	0·0630	34	0·1959	59	0·4997	84	1·1643
9	0·0659	35	0·2038	60	0·5178	85	1·2023
10	0·0689	36	0·2119	61	0·5364	86	1·2413
11	0·0721	37	0·2204	62	0·5556	87	1·2815
12	0·0753	38	0·2291	63	0·5755	88	1·3228
13	0·0788	39	0·2381	64	0·5959	89	1·3652
14	0·0823	40	0·2475	65	0·6170	90	1·4088
15	0·0861	41	0·2571	66	0·6388	91	1·4537
16	0·0899	42	0·2672	67	0·6612	92	1·4998
17	0·0940	43	0·2775	68	0·6843	93	1·5471
18	0·0982	44	0·2882	69	0·7081	94	1·5958
19	0·1027	45	0·2993	70	0·7327	95	1·6457
20	0·1073	46	0·3108	71	0·7580	96	1·6971
21	0·1121	47	0·3226	72	0·7841	97	1·7498
22	0·1171	48	0·3349	73	0·8109	98	1·8039
23	0·1223	49	0·3476	74	0·8386	99	1·8595
24	0·1278	50	0·3607	75	0·8671	100	1·9170
25	0·1335						

This Table is computed from Regnault's experiments, and is taken from Dixon's "Treatise on Heat" (p. 257).

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THE END.

ADDITIONAL ERRATA IN PART I. Second Edition.

Page 41, 4 lines from top, for *below*, read *above*.

" 126, 21 " " for *inelastic*, read *elastic*.

" 199, Transpose the first two terms of the proportion.

" 250, 5 lines below the table, for *twentieth*, read *sixth*.

" 275, 15 lines from top, add, *and subtracting the product from the last-mentioned temperature.*

" 388, 12 " " for *coil* read *cell*.

" 392, 9 " " for 1838, read 1858.

" 395, 15 " " for *directly*, read *inversely*.

ADDITIONAL ERRATA IN PART II. Second Edition.

Page 159. In table of sulphurous acid, first line, for 2 *or* 1·0, read 1 *or* 0·5.

" 183. In table of sulphuretted hydrogen, for $\begin{matrix}2 \textit{ or } 1·0=0·069\\ 1 \textit{ or } 0·5=1·105\end{matrix}$ read $\begin{matrix}1 \textit{ or } 0·5=1·105\\ 2 \textit{ or } 1·0=0·069\end{matrix}$

" 223, 7 lines from top, for 54·3, read 53·3.

" 276, 21 lines from bottom, for N_2C_6, read N_3C_6.

" 290, 7 " " of text, for xxii., read xii.

" 362. In first table, for 13·3, read 11·8; and for 11·8, read 13·3.

" 365, 7 lines from bottom, for 60·21, read 60·79; and for 39·79, read 39·21.

" 399, 12 " top, for 3 PbO,BO_3, read 3 $PbO,2\,BO_3$.

" 484, 4 " bottom of text, for 273·7, read 173·7.

" " First line of note, for 93·4, read 115·8.

" " Last line of note, for 22·4, read 44·8.

" 485, 12 lines from top, for 39·5, read 59·5.

" 540, 10 " bottom, insert *other* before *metal*.

" 546, 13 " top, for 2 Fe_2S_3, read Fe_2S_3.

" 591, 4 " " for(CuSn), read (Cu_6Sn).

" 861, 23 " " for 22·4, read 44·8.

" " In table, the number for rhodium should be 52·1.

ERRATA IN PART III. Second Edition.

Page 10, 6 lines from top, dele *in*.

" 32, 10 " bottom, for HO,C_2HO_4, read HO,C_2HO_3.

" 43. In table, the formula for thiacetic ether should be $(C_4H_3O_2)\,(C_4H_5)S_2$.

" 57. In each equation for Isatin, for 2 (KO,C_2O_4) read 2 $(2\,KO,C_2O_4)$.

" 82, 21 lines from bottom, for 15160 read 12630.

" 159, 7 lines from top, for xlv. read xliii.

" 181, 3 " top " *measures*, read *weights*.

" 197. First line, dele 2 HO, in the formula.

" 219. In table (in some copies) in the formula for dimethiodide of tin, for $Sn_2\left\{\begin{matrix}(C_2H_3)_2\\ I_2\end{matrix}\right\}$ read $Sn_2\left\{\begin{matrix}(C_2H_3)_2\\ I\end{matrix}\right\}$.

" " In the formula for stannic iodotrimethide, for $(C_4H_3)_3$ read $(C_2H_3)_3$.

" 221, 5 lines from bottom, read the composition of boric dioxyethide as follows; $B\left\{\begin{matrix}C_4H_5\\ (C_4H_5O_2)_2\end{matrix}\right.$.

" 246, 17 lines from top, for *iodide* read *chloride*.

" 314, 16 " top for 3 $HO,C_{14}H_3O_{11}$, read 3 $HO,C_{14}HO_{11}$.

" 318. Last line of table, for $C_{18}H_{17}O_4$, read $C_{18}H_{17}O_3$.

" 326. The general formula for the ketones should be $\left.\begin{matrix}C_{2n}\ H_{2n-1}O_2\\ C_{2n-2}H_{2n-1}\end{matrix}\right\}$.

" 332. In the table, the melting point of butyric, valeric, and caproic acids should be given as *below* 0° F.

" 344, 6 lines from top, for 19 *parts or* 1 *atom*, read 57 *parts or* 3 *atoms*.

" 346, 18 lines from bottom, for 115°, read 145°.

" 364, 13 " top, dele *oleic is metameric with ricinoleic acid*.

" 371, 8 " " add + HO to the end of the equation.

" 372. First line, *for* HO (in formula) read 2 HO.

Page 391, 15 lines from top, for *acetate*, read *acetic*.
,, 419. In formula for benzamide, for $\}\,O_2$, read $\}\,N$.
,, 426. In second equation, both times, for $(C_{20}H_{16}O_4)''$, read $(C_{20}H_{14}O_4)''$.
,, 431. Last line but one, insert 2 before H_2O_2.
,, 438, 4 lines from bottom, for *electro-negative*, read *electro-positive*.
,, 451, 13 ,, ,, for C_{14} read C_{12}.
,, 454, 9 ,, top, in formula for platosopyridine, for pt., read Pt.
,, ,, 17 ,, ,, for pt., read Pt.
,, 475, 4 ,, bottom, for $2\,C_{12}H_7N,HCl$, read $2\,(C_{12}H_7N,HCl)$.
,, 478, 6 ,, ,, for $(C_2O_2)''_2$, read $(C_2O_2)''$ in equation.
,, 496, 13 ,, top, transfer the sentence beginning—*It does not appear*, to p. 495, 7 lines from top.
,, 497. In the formulæ for opiammon and teropiammon, for N_2, read N, throughout.
,, 502. Last line but one of table, for 6 Aq, read 4 Aq.
,, ,, Last line of table, for 6 Aq, read 8 Aq; dele *moderately*.
,, 511. In the equation, for 2 AgI, read AgI.
,, 525. Last line, for 3 HCl, read 2 HCl.
,, 540, 5 lines from top, for $+Cl_2 = 2\,HCl$, read $+2\,Cl_2 = 4\,HCl$.
,, 544, 18 ,, bottom, for 2 Aq, read 4 Aq.
,, 583. In table, formula for allyloxamic ether, for C_4O, read C_4O_2.
,, ,, ,, next line, for C_2O, read C_2O_4.
,, 607. Last line but one in note, for O_{14}, read O_{40}.
,, 611, 6 lines from top, for $(NO_4)_2\,O + 2\,Aq$, read $(NO_4)_2O_4 + 2\,Aq$.
,, 612, 7 ,, bottom, for HO,C_{14}, read HO,C_{16}.
,, 655. Last line (in some copies), for $KO,C_{14}HO_3$, read $KO,C_{14}H_5O_3$.
,, 664. In formula for sulphonaphthalin, for $C_{40}H_{14}S_2O_2$, read $C_{40}H_{14}S_2O_4$.
,, 690. In table, for Fe_2, read Fe_3.
,, 695. Last line but one of table, for HgScy, read 2 HgScy.
,, 731. First line, for *alloxan*, read *alloxantin*.

ADDITIONAL ERRATA IN PART III.

Page 41, 3 lines from bottom, the formulæ should be

$$\left.\begin{matrix} C_4H_5 \\ C_4H_5 \end{matrix}\right\} O_2; \quad \left.\begin{matrix} C_2H_3 \\ C_4H_5 \end{matrix}\right\} O_2; \quad \left.\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix}\right\} O_2$$

,, 49, lines 22 and 23 from top, dele *arsenides and antimonides*.
,, 51, 7 lines from top, after *phosphides*, insert *arsenides and antimonides*.

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